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A NEW BAND SYSTEM (CORDES BANDS) OF IODINE

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(Communicated by Dr. R. K. Asundi, F.A.SC.)

Cordes has recorded the absorption spectrum of iodine vapour in the region 1950 to 1500 A employing a vacuum fluorite spectrograph having a dispersion of 2·3 A/mm. at 1700 A which naturally falls rapidly on the long wavelength side. He used for the absorption cell a tube 80 cm. long with fluorite windows. Iodine is kept in a side tube that is attached to the absorption cell. By changing the temperature of the side tube the vapour pressure of iodine vapour in the absorption cell could be changed in a definite way. He photographed the absorption spectrum at different pressures ranging from 3×10^{-4} mm. to a pressure of 0·08 mm. The lower pressure corresponds to $-36°$ C. A water-cooled hydrogen discharge tube was the source of the continuous radiation. Different sets of bands were obtained at different pressures. Bands about 53 in number on the shorter wavelength side which are given in Table I of Cordes paper[1] were analysed by him into eight different systems which all involve transitions from ground state to different excited electronic states above 56,000 cm.$^{-1}$ Another group of bands about 110 in number recorded in Table II of Cordes paper have not been analysed by him. He is of the opinion that they form the extension in one progression towards shorter wavelengths of Pringsheim-Rosen, Kimura-Miyanishi (P. R., K. M.)[2] bands which lie in the region 2700 A to 2000 A. But this is not probable because although the successive differences of the bands are of the expected order, they are completely spasmodic and do not exhibit even that small regularity of decrease which is present in P-R, K-M bands as analysed by Sponer and Watson.[2c] This group of about 110 bands seems to consist of two sets of bands with a gap of about 18 A in between : an extensive system of about 94 bands from 1950 to 1794 A occurring at a distance of about 2 A from one another and a few bands about 16 in number from 1776 to 1697 A. Further it appears that the second set probably belongs to one of the eight systems analysed by Cordes. The present paper deals with the analysis of the first extensive system of 94 bands between 1950 to 1794 A. These bands make their appearance, according to Cordes, at a pressure of 3×10^{-3} mm. and are completely developed at higher pressures (8×10^{-2} mm.). The heads of the bands are not quite recognisable, though they appear shaded towards red at higher pressures.

The wavelengths and wave numbers of these 94 bands from Cordes paper are given in Table I. Here the wavelengths are however given correct to a tenth of an Angstrom and wave-numbers are given in whole numbers only. The bands are arranged in a V′, V″ scheme as given in Table II and are well represented by the equation:

$$\nu = 51683 + (164{\cdot}5\,V' - 0{\cdot}6\,V'^2 - 0{\cdot}0035\,V'^3) - (213{\cdot}6\,V'' - 0{\cdot}6\,V''^2),$$

which in a physically more significant form becomes

$$\nu = 51707{\cdot}55 + \{165{\cdot}1\,(V' + \tfrac{1}{2}) - 0{\cdot}595\,(V' + \tfrac{1}{2})^2 - 0{\cdot}0035\,(V' + \tfrac{1}{2})^3\} - \{214{\cdot}2\,(V'' + \tfrac{1}{2}) - 0{\cdot}6\,(V'' + \tfrac{1}{2})^2\}.$$

The respective V′, V″ values and O − C values of all the bands are given in Table I. It can be seen that some bands marked (*b*) can be placed at two places in the V′, V″ scheme. Probably these values recorded by Cordes correspond to the mean value of two bands which might have caused some blending being very near to each other. This seems to be genuine because just for these bands the O − C values (Table I) and the $\Delta G_{v''}$ values (Table II) are abnormal. For all the other bands the O − C values are reasonable if one takes into consideration the fact that the band heads are not quite recognisable, and therefore difficult to locate and measure. This may also be partly responsible for the irregularities in the ΔG_v values, but it may be mentioned that the irregularities met with can be deemed slight in comparison with those obtained in the analysis of other band systems of the molecule.

In keeping with the low temperatures at which the absorption is measured only a few vibrational levels of the ground state are excited. The V″ = 0, 1 and 2 progressions are well developed and the existence of a few bands with high V′ values involving V″ = 3 and 4 indicates the nature of the Condon parabola representing a moderate change in ω_e and r_e values.

The expression $214{\cdot}2\,(V'' + \tfrac{1}{2}) - 0{\cdot}6\,(V'' + \tfrac{1}{2})^2$ is very close to that of the ground state of iodine molecule[3] and this proves that Cordes bands are due to a transition from the ground state to an excited state with a frequency of 165·1 cm.$^{-1}$ and situated at 51683 cm.$^{-1}$ above the ground level. The state which gives P.R. and K.M. bands has $\omega_e \sim 90$ cm.$^{-1}$ according to Sponer and Watson.[2c, d] A preliminary attempt has shown that only a few bands if at all, on the extreme short wave side of K. M. bands, can come in the V″, V′ scheme of Cordes bands with high V″ values. The above interpretation is supported by the fact that there are five groups of bands in

TABLE I

λ	ν	(V′, V″)	O−C
1948·1	51333	3, 4	+ 8
1945·9	51390	2, 3	+16
1944·7	51423	1, 2	+ 1
1942·7	51475	0, 1	+ 5
1940·8	51527	3, 3	− 9
1938·6	51584	2, 2	− 1
1936·7	51635	1, 1	+ 1
1934·9	51683	0, 0	0
1932·8	51739	3, 2	− 7
1930·6	51799	2, 1	+ 2
1928·7	51849	1, 0	+ 2
1926·6	51904	4, 2	− 2
1924·7	51956	3, 1	− 2
1922·6	52013	2, 0	+ 3
1920·7	52065	5, 2	0
1918·6	52120	4, 1	+ 2
1916·6	52175	3, 0	+ 4
1914·7	52227	6, 2	+ 4
1912·9	52277	5, 1	0
1911·0	52330	4, 0	− 1
1909·0	52383	7, 2	+ 4
1907·1	52435	6, 1	0
1905·2	52489	5, 0	− 1
1903·5	52535	8, 2	+ 1
1901·6	52588	7, 1	− 3
1899·8	52637	6, 0	−10
1897·8	52692	9, 2	+ 4
1896·0	52743	8, 1	− 3
1894·3[b]	52790	(7, 0), (11, 3)	−14, +10
1892·3	52847	10, 2	+ 7
1890·8	52887	9, 1	−12
1888·9[b]	52940	(8, 0), (12, 3)	−19 +11
1887·0	52994	11, 2	+ 4
1885·2	53048	10, 1	− 4
1883·7[b]	53088	(9, 0), (13, 3)	−24, +11
1881·8	53140	12, 2	0
1880·0	53193	11, 1	− 9
1878·1[b]	53248	(10, 0), (14, 3)	−16, +24
1876·4	53295	13, 2	+ 7
1874·5	53348	12, 1	− 4
1872·9[b]	53394	(11, 0), (15, 3)	−21, +26
1871·2	53442	14, 2	+ 8
1869·5	53491	13, 1	− 8
1867·5[b]	53548	(12, 0), (16, 3)	−17, +36
1866·0	53591	15, 2	+12
1864·3	53639	14, 1	− 7
1862·8[b]	53682	(13, 0), (17, 3)	−30, +28
1861·0	53733	16, 2	+11
1859·4	53782	15, 1	− 9
1857·8[b]	53827	(14, 0), (18, 3)	−32, +33
1856·1	53876	17, 2	+12
1854·5	53923	19, 3	− 9
1852·9[b]	53969	(16, 1), (21, 4)	+35, −36
1851·4	54014	18, 2	+10
1849·6	54066	20, 3	− 3
1848·2[b]	54107	(22, 4), (17, 1)	−22, +31
1846·6	54153	19, 2	+10
1845·0	54200	21, 3	− 5

TABLE 1.—(*Contd.*)

λ	ν	(V′, V″)	O−C
1843·5[b]	54245	(23, 4), (18, 1)	−16, +29
1841·8	54294	17, 0	+ 5
1840·4	54337	22, 3	− 2
1839·1[b]	54376	(19, 1), (24, 4)	+21, −16
1837·5[b]	54422	(18, 0), (21, 2)	− 7, +6
1836·1	54465	23, 3	− 6
1834·7[b]	54505	(20, 1), (25, 4)	+13, −16
1833·2	54549	22, 2	− 1
1831·6	54597	24, 3	− 4
1830·2	54638	21, 1	+10
1828·9	54679	23, 2	− 3
1827·3	54725	25, 3	− 5
1825·9	54767	22, 1	+ 6
1824·6	54808	24, 2	− 4
1823·0	54854	26, 3	− 3
1821·7	54895	23, 1	+ 1
1820·1	54941	25, 2	0
1818·9	54979	22, 0	+ 5
1817·5	55021	24, 1	− 3
1816·0	55066	26, 2	− 2
1814·7	55105	23, 0	− 2
1813·3	55149	25, 1	− 4
1812·1	55185	27, 2	− 9
1810·5	55233	29, 3	+ 5
1809·3	55271	26, 1	− 9
1808·0	55311	28, 2	− 6
1806·7	55351	30, 3	+ 3
1805·3	55391	27, 1	−14
1804·0	55432	29, 2	− 7
1802·6	55475	31, 3	+ 9
1801·1	55522	28, 1	− 7
1798·9	55591	32, 3	+ 8
1797·6	55630	27, 0	+11
1796·6	55661	29, 1	+10
1795·5	55695	31, 2	+18
1794·3	55734	28, 0	− 8

emission with successive separation of about 165 cm.$^{-1}$, which can only be explained due to transitions from the state at 51683 cm.$^{-1}$ having $\omega = 165$ cm.$^{-1}$, to five different repulsive states dissociating into $^2P_{3/2} + {}^2P_{3/2}$, $^2P_{3/2} + {}^2P_{1/2}$ and $^2P_{1/2} + {}^2P_{1/2}$ iodine atoms[9]. Therefore, the Cordes bands and P.R.K.M. bands come from two different states, the state giving rise to Cordes bands being the higher of the two.

Graphical extrapolation which is however a long one, gives the value 59000 ± 800 cm.$^{-1}$ or about $7{\cdot}28 \pm 0{\cdot}18$ volts, for the convergence limit of Cordes bands. The dissociation energy of the molecular state is thus 7317 ± 800 cm.$^{-1}$ Linear extrapolation for convergence gives the value 63143 cm.$^{-1}$ or about 7·8 volts which is the upper limit. The convergence limit for P.R.K.M. bands as found by Sponer and Watson[2c] is also about

TABLE II

V'' / V'	0		1		2		3		4	ΔG'
0	51683	*208*	51475							
	166		*160*							*163*
1	51849	*214*	51635	*212*	51423					
	164		*164*		*161*					*163*
2	52013	*214*	51799	*215*	51584	*194*	51390			
	162		*157*		*155*					*158*
3	52175	*219*	51956	*217*	51739	*212*	51527	*194*	51333	
	155		*161*		*165*					*161*
4	52330	*210*	52120	*216*	51904					
	159		*157*		*161*					*159*
5	52489	*212*	52277	*212*	52065					
	148		*158*		*162*					*156*
6	52637	*202*	52435	*212*	52227					
	153		*153*		*156*					*154*
7	52790[b]		52588	*205*	52383					
	150		*155*		*148*					*151*
8	52940[b]		52743	*208*	52535					
	148		*144*		*157*					*150*
9	53088[b]		52887		52692					
	160		*161*		*155*					*159*
10	53248[b]		53048	*201*	52847					
	146		*145*		*147*					*146*
11	53394[b]		53193	*199*	52994		52790[b]			
	153		*155*		*146*		*150*			*151*
12	53548[b]		53348	*208*	53140		52940[b]			
	134		*143*		*145*		*148*			*143*
13	53682[b]		53491		53295		53088[b]			
	145		*148*		*147*		*160*			*147*
14	53827[b]		53639	*197*	53442		53248[b]			
			143		*149*		*146*			*146*
15	..		53782		53591		53394[b]			
					142		*154*			*148*
16	..		53969[b]		53733		53548[b]			
			138		*143*		*134*			*138*
17	54294		54107[b]		53876		53682			
	128		*138*		*138*		*145*			*137*
18	54422[b]		54246[b]		54014		53827[b]			
			131		*139*					*135*
19	..		54375[b]		54153		53923			
			129				*143*			*136*
20	..		54505[b]		..		54066			
			133				*134*			*134*
21	..		54638		54422[b]		54200		53969[b]	
			129		*127*		*137*		*138*	*133*
22	54979	*212*	54767	*218*	54549	*212*	54337		54107[b]	
	126		*128*		*130*		*138*		*138*	*130*
23	55105	*210*	54895	*216*	54679	*214*	54465	*220*	54245[b]	
			126		*129*		*132*		*130*	*131*
24	..		55021	*213*	54808	*211*	54597		54376[b]	
			128		*133*		*128*		*129*	*130*
25	..		55149	*208*	54941	*218*	54725	*220*	54505[b]	
			122		*125*		*129*			*125*
26	..		55271	*205*	55066	*212*	54854			
			120		*119*					*120*
27	55630	*239*	55391	*206*	55185		..			
			131		*126*					*128*
28	55734	*212*	55522	*211*	55311					
			139		*121*					*130*
29	..		55661	*229*	55432	*201*	55233			
							118			*118*
30	..		..		..		55351			
							124			*124*
31	..		..		55695	*220*	55475			
							116			*116*
32	..		..		..		55591			
ΔG''		*214*		*211*		*210*		*211?*		

* In calculating the average ΔG'' values the abnormal ΔG'' values which are mostly due to bands marked *b* are neglected.

60,200 cm.$^{-1}$ or about 7·45 volts. Thus the molecular state giving rise to Cordes bands, and that giving rise to K.M.P.R. bands arise from the same dissociation products.

The question is what are the probable dissociation products ? Now the ground state of the molecule dissociates into two normal I atoms in $^2P_{3/2}$ state at 12437 cm.$^{-1}$ (1·535 volts). The atomic term difference $^2P_{3/2} - {}^2P_{1/2}$ being 7600 cm.$^{-1}$ the dissociation level $^2P_{3/2} + {}^2P_{\frac{1}{2}}$ will therefore be at 20037 cm.$^{-1}$ and that of $^2P_{\frac{1}{2}} + {}^2P_{\frac{1}{2}}$ at 27637 cm.$^{-1}$ The resonance line $5p$, $^2P_{3/2} \leftrightarrow 6s$, $^4P_{5/2}$ of iodine atom lies at 1830 A corresponding to an energy of 6·74 volts or 54632 cm.$^{-1}$[14] Thus the level $^2P_{3/2} + {}^4P_{5/2}$ lies at 54632 + 12437 = 67069 cm.$^{-1}$ or 8·28 volts. If the dissociation products are to be *neutral* (though excited) atoms, there can be no level of dissociation products between 67069 and 27637 cm.$^{-1}$ The maximum value of the convergence limit of the Cordes absorption bands is 63143 cm.$^{-1}$ or 7·8 volts. Thus it is evident that the dissociation products are not neutral atoms. The only other possibility is that they are I^- ($^1S_0$) + I^+ ($^3P_2$), negative and positive ions in their ground states. If we assume that this is true and that the electron affinity[5] of iodine atom is 3·14 ± 0·07 volts, the ionisation potential of the iodine atom can be calculated as 8·9 ± 0·2 volts. This agrees with the ionisation potential experimentally obtained which varies from 8 to 10·5 volts according to different observers.[6] Thus the possible dissociation products are very likely I^+ ($^3P_2$) + I^- ($^1S_0$). In support of this view there is the experiment of Ludlam and West[7] which shows appreciable conductivity in iodine vapour excited by wavelengths below 1850 A (above 54100 cm.$^{-1}$). However the excitation being not monochromatic it is not possible to calculate the exact energy of the level $I^+ + I^-$ from their experiments.

The next problem is to find the probable electronic terms and electronic configurations of the two molecular states. Mulliken[8] has given the term scheme of the iodine molecule. The ground state of the molecule, $^1\Sigma_g^+$ or O_g^+ has the electronic configuration σ_g^2, π_u^4, π_g^4. [A transition from this to σ_g^2, π_u^4, π_g^3, σ_u (O_u^+) and (1_u) gives the visible and near infra-red absorption bands.] The probable electronic configuration (as Mulliken has suggested for P.R.K.M. bands), for the two states that give Cordes and P.R.K.M. bands seems to be σ_g, π_u^4, π_g^4, σ_u. The probable electronic states from this are $^1\Sigma_u^+$ and $^3\Sigma_u^+$ if the coupling is of case (*a*) or (*b*) type and O_u^+, 1_u, O_u^- if the coupling is of case (*c*) type.[8] $^1\Sigma_u^+$ of case (*a*) type is to be correlated with O_u^+ of case (*c*) type and $^3\Sigma_u^+$ of case (*a*) type to be correlated with 1_u and O_u^- of case (*c*) type. Cordes as well as Mulliken have attributed $^1\Sigma_u^+$ to the state that gives rise to P.R.K.M. bands. The dissociation products according to Cordes are I^- ($^1S_0$) + I^+ ($^3P_2$). But the combination of these two atomic

terms gives only triplets but not singlets. Thus the attribution of a singlet state $^1\Sigma_u^+$ according to strict case (*a*) or (*b*) type is not suitable. In a heavy molecule like iodine the tendency to case (*c*) type coupling is however greater than to case (*a*) or (*b*) type. Then Ω becomes a good quantum number and the distinction between singlets and triplets loses its meaning. As already mentioned above the probable electronic states according to case (*c*) type from the electronic configuration $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$ are O_u^+, 1_u and O_u^-. In absorption a transition cannot take place from the ground state to O_u^- because of $+ \rightarrow -$ prohibition rule. Thus O_u^+ and 1_u seem to be the two electronic states that give rise to Cordes bands and K.M. bands respectively O_u^+ being of greater energy than 1_u. O^+ and 1 states are among the states that will be possible from case (*c*) type coupling of $I^-(^1S_0) + I^+(^3P_2)$. Thus we conclude that Cordes bands belong to a transition from ground state to O_u^+ state and P.R.K.M. bands are due to a transition from ground state to 1_u state.

My thanks are due to Prof. R. K. Asundi, for guidance and help.

Summary

A new band system involving a frequency of 165·1 cm.$^{-1}$ in the excited state of the molecule is discovered in the absorption spectrum of iodine as measured by Cordes. This locates an electronic level at 51683 cm.$^{-1}$ above the ground level. The P-R, K-M bands form very probably a different system with a lower electronic level for their excited state. The dissociation products of the initial states of both the systems are however identical, *viz.*, $I^-(^1S_0) + I^+(^3P_2)$. The nature of the transitions giving rise to these two systems is discussed.

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EMISSION BANDS OF HALOGENS

Part I. Iodine Bands arising in 0_u^+ State at 51683 cm.$^{-1}$

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Introduction

In a previous communication on the emission bands of fluctuation type in the spectrum of iodine,[1] the existence of two wavenumber differences (about 214 cm.$^{-1}$ and 154 cm.$^{-1}$) among the bands in the region 4,800 to 3,450 A was pointed out. It was also suggested that the bands are probably due to the diatomic molecule I_2. Since then the bands have been further investigated with instruments of bigger dispersion and greater resolving power. In the meanwhile a new band system[2a] in the absorption spectrum of iodine recorded by Cordes[2b] has been reported. This system has for its excited electronic state a frequency of the order of 165 cm.$^{-1}$ This has led to an interpretation of such of the emission bands which involve a wavenumber difference of this order of magnitude. The present paper deals with this interpretation. General experimental details and description of the observed emission spectrum from 6700 A to 2400 A are given with wavelength data on the maxima of the bands interpreted.

Experimental Details

A quartz tube 10 cm. in length and 2 cm. in diameter with fused-on clear windows, and containing some resublimed iodine crystals is attached to an evacuating apparatus. After evacuating it is excited by high frequency oscillations using tin foils as external electrodes. The tube was gently heated until no impurity spectra could be detected after which it was sealed off. The high frequency oscillations used for exciting the discharge were obtained from a modified Hartley oscillatory circuit using a Telefunken 'Re 134' valve. The frequency of the oscillations used is about 900 kc/sec. The colour of the discharge was pinkish white. In the visible region the spectrum was photographed on a constant deviation glass spectrograph and a 3-prism glass Steinheil spectrograph. In the ultraviolet region a Medium Hilger quartz spectrograph and an E_1-Hilger quartz Littrow spectrograph were employed. The dispersion of the Steinheil spectrograph is about 6·5 A/mm.

at 4060 A and about 12·2 A/mm. at 4510 A. The E_1 quartz spectrograph has a dispersion of 4·2 A/mm. at 2860 A and about 11·2 A/mm. at 3920 A. Super Panchro-Press P 1200 and Process Regular B-20 Kodak plates were used. Process Regular B-20 plates proved to be more useful in the region 4500–2000 A as they gave better contrast than the other plates.

It is found that the nature of the spectrum (6700–2400 A) obtained by the above method does not differ from that obtained by exciting flowing iodine vapour through an uncondensed transformer discharge.

General Description of the Spectra Obtained

In the region 6700–5000 A discrete bands degraded towards red and identical with the well-known visible absorption bands of iodine were obtained. These were, however, not followed by any continuum as in the absorption bands. From 4800–2400 A, groups of diffuse bands were obtained. Of these the wavelengths and wavenumbers of the intensity maxima of the bands between 4800–3450 A only were published in *Nature*.[1]

The wavelengths and wavenumbers of the intensity maxima of the bands in the region 4154–3978 A and 2712–2687 A which only will be discussed in this paper are given in Table I. The intensity values given in the table

Table I

Emission as obtained in present experiments					Fluorescence	
Group	Intensity	λ in air	ν in vac.	Average Δν	McLennan λ in air	Oldenberg λ in air
I	6	4154·4	24064		(4170) ? A single broad band from 4130 to 4015	4007 (10)
	5	4124·2	24240			
	8	4094·6	24416			
	7	4067·6	24578	164·5		
	8	4044·6	24717			
	8	4018·0	24881			
	3	3991·1	25049			
II	8	3945·6	25338	169	3925	3925 (10)
	3	3919·4	25507			
III	6	3879·9	25767	161	3870	3866 (8)
	6	3855·8	25928			
IV	3	3821·8	26158	164	3800	3813 (7)
	4	3798·0	26322			
V	4	2712·0	36862	168	2715	
	3	2699·6	37032		2697	
	4	2687·5	37198		2685	

correspond to the visually estimated relative intensities of these bands obtained on the Process Regular plate taken on the E_1 quartz spectrograph. The wavelengths of the bands between 4154 A and 3798 A correspond to mean values obtained from a number of plates taken on Steinheil, E_1 quartz and Medium quartz spectrographs. So they differ slightly from the values published in *Nature*[1] which correspond to the mean values obtained from plates on Steinheil and Medium quartz spectrographs only as by that time experiments on E_1 quartz spectrograph were not done.* The values of the three bands between 2712 and 2687 A are means of three readings on plates from E_1 quartz spectrograph. Plate XXV is a reproduction of the bands obtained.

Interpretation of the Bands

All these bands are diffuse and do not show any kind of structure with the instruments used. The wavenumber difference of successive bands in different groups is of the order of 165 cm.$^{-1}$ So these bands are probably due to a transition from a single electronic state with $\omega = 165$ cm.$^{-1}$ to different lower unstable states. The first group (*vide* Table I) consists of seven diffuse bands with an average wavenumber separation of 164·5 cm.$^{-1}$ The first of these bands is at 24064 cm.$^{-1}$ A new electronic level in iodine molecule with a frequency of 165 cm.$^{-1}$ has been recently reported.[2a] It lies at 51683 cm.$^{-1}$ above the ground level. A transition from the ground state to this level gives the absorption bands recorded by Cordes in the vacuum region.[2b] If this electronic state is the initial state which gives rise to the seven diffuse bands of the first group, the point on the lower potential energy curve, which lies vertically below the minimum of the upper potential energy curve, will be at (51683–24064) – 27619 cm.$^{-1}$ above the ground level of I_2. Now the dissociation level of $I(^2P_{3/2}) + I(^2P_{3/2})$ which is accurately known from the visible absorption bands is at 20037 cm.$^{-1}$[3] The atomic term difference $(^2P_{1/2} - {}^2P_{3/2})$ from Turner's[4] experiment is 7600 cm.$^{-1}$ So the dissociation level $I(^2P_{1/2}) + I(^2P_{1/2})$ lies at 27637 cm.$^{-1}$ It is thus possible to identify the lower state of the first group of seven bands as a repulsive state arising out of $I(^2P_{1/2}) + I(^2P_{1/2})$ and having a flat potential energy curve. So a transition from the stable electronic state ($\omega = 165$ cm.$^{-1}$) to the flat potential energy curve that dissociates into $I(^2P_{1/2}) + I(^2P_{1/2})$ atoms gives the first group of bands.

Each of the second, third, and fourth groups (Table I) consists of two bands with wavenumber separations 169 cm.$^{-1}$, 161 cm.$^{-1}$ and 164 cm.$^{-1}$

* Grouping of the bands has also to be changed slightly because of the data available from the recent experiments.

respectively. The two bands of each group overlap one another and give the appearance of a broad continuous band with two intensity maxima. This suggests that these bands are due to transitions from the stable electronic state ($\omega = 165\,\text{cm.}^{-1}$) to three different repulsive curves of three unstable states. The three points on the repulsive curves, which lie vertically below the minimum of the stable potential energy curve lie at (51683–25338) = 26345 cm.$^{-1}$, (51683–25767) = 25916 cm.$^{-1}$ and (51683–26158) = 25525 cm.$^{-1}$ respectively above the ground level. These repulsive states, which are slightly steep and almost parallel except at their common convergence limit, probably dissociate into $I(^2P_{1/2}) + I(^2P_{3/2})$ atoms whose dissoiation level lies at 20037 cm^{-1}.

The three diffuse bands of the fifth group in the ultraviolet lie at 2712·0 A (36862 cm.$^{-1}$), 2699·6 A (37032 cm.$^{-1}$), and 2687·5 A (37198 cm.$^{-1}$) with an average wavenumber separation of 168 cm.$^{-1}$ If this state also has the above stated stable electronic level as the upper state, the point on the lower potential energy curve that lies vertically below the stable state will be at (51683–36862) = 14821 cm.$^{-1}$ This state is also a repulsive state having a nearly flat curve dissociating into $I(^2P_{3/2}) + I(^2P_{3/2})$ level at 12437 cm.$^{-1}$ or 1·535 volts.

It is indeed satisfactory to find that this interpretation is moreover in accordance with the theoretical predictions as to the number and nature of the electronic levels of I_2. The different molecular electronic states and their nature can be worked out either by combining the two iodine atoms in normal and various excited states, or from the electronic configurations of the molecule as a whole. In neither case, however, can the excited energies be accurately calculated. Mulliken[5] has worked out the term scheme and electronic configurations for the predicted molecular states. Now the ground state of the iodine molecule is $^1\Sigma_g^+ (0_g^+)$ and the electronic configuration of the ten outer electrons is $\sigma_g^2, \pi_u^4, \pi_g^4$. The electronic state with $\omega = 165{\cdot}1\,\text{cm.}^{-1}$ at 51683 cm.$^{-1}$ is 0_u^+ state[2a] according to case (*c*) type coupling and can be correlated with $^1\Sigma_u^+$ of case (*a*) or (*b*) type. The electronic configuration of this state which is the initial state of all the bands interpreted here is $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$. This dissociates into $I^-(^1S_0) + I^+(^3P_2)$ ions.

The lower state of the bands in the first group, according to the present interpretation, dissociates into $I(^2P_{1/2}) + I(^2P_{1/2})$ atoms. The electronic states that are possible from the combination of such two atoms, according to case (*c*) type coupling, are 0_u^-, 1_u and 0_g^+. The only possible term out of these three, that can combine with the initial state 0_u^+, is 0_g^+. This 0_g^+ state can easily be correlated with $^1\Sigma_g^+$ of case (*a*) or (*b*) type which is one of the

states that can be derived from the electronic configuration $\sigma_g^2, \pi_u^4, \pi_g^2, \sigma_u^2$. (From this configuration the states $^1\Sigma_g^+$, $^1\Delta_g$, $^3\Sigma_g^-$ are possible).[5] Thus a transition from $\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$; 0^+ ($^1\Sigma_u^+$) to $\sigma_g^2, \pi_u^4, \pi_g^2, \sigma_u^2$; 0^+_g ($^1\Sigma^+_g$) gives the seven diffuse bands of group I.

We have interpreted that the next three groups have their lower states dissociating into $I(^2P_{3/2}) + I(^2P_{1/2})$. The possible electronic states from the combination of these two atomic terms, according to case (*c*) type are 2_g, 2_u, 1_g, 1_u, 1_g, 1_u, 0_g^+, 0_u^+, 0_g^-, 0_u^-. Of all these the only terms that can combine with the state 0_u^+ are 0_g^+, 1_g and 1_g. These respectively correspond to the final states of the bands in second, third and fourth groups. The first two terms 0_g^+ and 1_g which correspond to the final states of second and third groups can be correlated with $^3\Sigma_g^-$ of case (*a*) or (*b*) type[5] which can be derived from the same electronic configuration $\sigma_g^2, \pi_u^4, \pi_g^2, \sigma_u^2$, as the $^1\Sigma_g^+$ state discussed above. Had it been a case (*a*) or (*b*) type coupling, however, the first two transitions would not have been possible because of $\Sigma^+ \leftarrow|\rightarrow \Sigma^-$ prohibition rule. The occurrence of these two transitions is therefore a clear proof of the existence of case (*c*) type coupling in the iodine molecule, by which Ω becomes a good quantum number and Λ and Σ lose their significance. The third state 1_g which is the lower state of the bands in the fourth group, can be correlated with $^1\Pi_g$ of case (*a*) type.[5] The electronic configuration of this state is $\sigma^2_g, \pi^3_u, \pi^4_g, \sigma_u$. Thus the second, third and fourth groups of bands definitely arise from the following transitions:

II Group: $-\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$; $0_u^+(^1\Sigma_u^+) \rightarrow \sigma^2_g, \pi^4_u, \pi^2_g, \sigma^2_u$; 0^+_g ($^3\Sigma_g^-$)

III Group: $-\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$; $0_u^+(^1\Sigma_u^+) \rightarrow \sigma_g^2, \pi_u^4, \pi_u^2, \sigma_u^2$; 1_g

IV Group: $-\sigma_g, \pi_u^4, \pi_g^4, \sigma_u$; $0^+_u(^1\Sigma_u^+) \rightarrow \sigma^2_g, \pi^3_u, \pi^4_g, \sigma_u$; 1_g ($^1\Pi_g$)

The fifth group consisting of three bands has a lower state dissociating into $I(^2P_{3/2}) + I(^2P_{3/2})$. The possible electronic terms that arise from the combination of these two atomic terms are: 3_u, 2_u, 2_g, 1_u, 1_g, 1_u, 0_u^-, 0_g^+, 0_u^- 0_g^+. Of these, the terms that can combine with 0_u are only 0_g^+, 0_g^+, 1_g, Among these three, one 0_g^+ corresponds to the ground state of the iodine molecule. The remaining two states 0_g^+ and 1_g, of which the former lies higher of the two, can be corrected with $^3\Pi_g$ of case (*a*) or (*b*) type which can be derived from the electronic configuration $\sigma_g^2, \pi_u^3, \pi_g^4, \sigma_u$. We will attribute the term 0_g^+ ($^3\Pi_g$) to the repulsive state that forms the final level of the bands of group V. The transition can be written as:

$$\sigma_g, \pi_u^4, \pi_g^4, \sigma_u \cdot 0_u^+(^1\Sigma_u^+) \rightarrow \sigma_g^2, \pi_u^3, \pi_g^4, \sigma_u \cdot 0_g^+ (^3\Pi_g).$$

Fluorescence Bands

McLennan[6] in 1913, and Oldenberg[7] in 1923 have obtained some fluorescence bands in this region by exciting iodine vapour with quartz mercury lamp. According to McLennan, the Hg lines λ 1942·3 and λ 1849·6 are responsible for the ultraviolet fluorescence. McLennan could get only a single broad continuous band extending from 4130 to 4015 A instead of the seven bands in the first group and one band each for the next three groups. This might probably be because of the low dispersion instruments they used. The results of McLennan and Oldenberg are included in Table I. The numbers in brackets are the intensity values given in Oldenberg's paper. The explanation of these fluorescence bands is now simple. By illuminating the iodine vapour with wavelengths between 1950 and 1840 A, the molecules in the ground state can easily go to the stable electronic state 0_u^+ at 51683 cm.$^{-1}$ Transitions from this 0_u^+ state to different lower repulsive states, give the fluorescent bands similar to those obtained in emission.

Summary

Among the diffuse fluctuation bands observed in the emission spectrum of iodine, there are five groups each of which involves a frequency difference of about 165 cm.$^{-1}$ among the component bands. An interpretation of these five groups is given, which shows that they are due to transitions from a common initial level to five different final levels. The initial level is identified with the newly discovered level 0_u^+ at 51683 cm^{-1}. The five different final levels are identified with just those states whose energies and nature can be calculated theoretically. All these are repulsive states with potential energy curves of varying slopes.* The occurrence of bands (3945·6 and 3919·4 A) in the second group and of bands (3879·9 and 3855·8 A) in the third group clearly shows that the coupling conditions in I_2 are of Hund's case (*c*).

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* Fluorescence bands observed by McLennan and Oldenberg find a similar interpretation.

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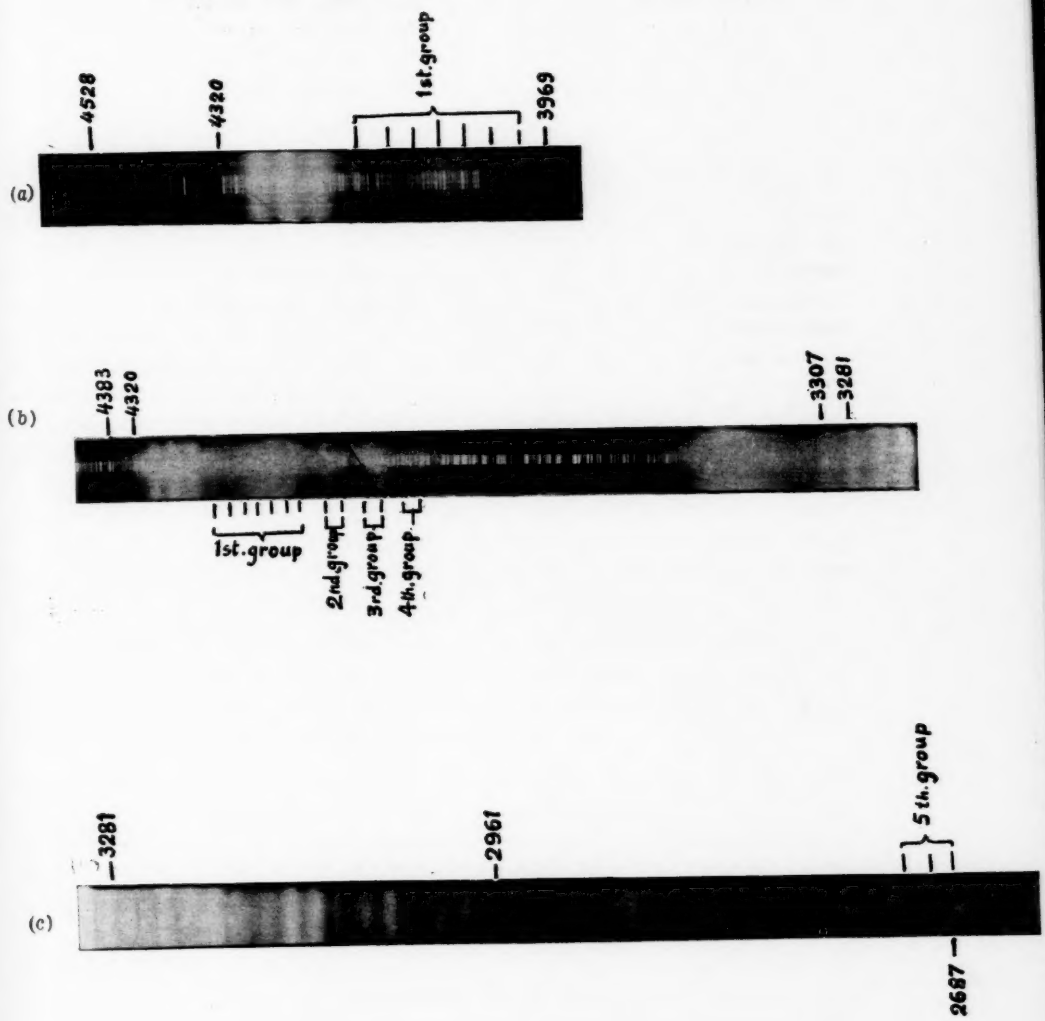
ILLUSTRATION TO PLATE

The plate shows the emission spectrum of iodine vapour excited by high frequency oscillations.

Spectrum (*a*) is taken on a 3 prism glass Steinheil spectrograph. The bands of the first group (Table I) are marked.

The spectra (*b*) and (*c*) are taken on an E_1 quartz spectrograph. The bands of the first, second, third and fourth groups are marked in spectrum (*b*), and those of the fifth group are marked in spectrum (*c*).


(a)
4528
4320
1st.group
3969
(b)
4383
4320
3307
3281
1st.group
2nd.group
3rd.group
4th.group
(c)
3281
2961
5th.group
2687

CONDENSATION OF ALDEHYDES WITH AMIDES

Part XII. Condensation of Benzaldehyde and *o*-Chlorobenzaldehyde

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Pandya and Miss Pandya have shown that the aldehyde-malonic acid condensation is very favourably influenced by a chlorine or a bromine atom on the ring of the aldehyde.[1] In the present paper an effort is made to find out if the aldehyde-amide condensation is similarly influenced by one chlorine atom on the aromatic ring of the aldehyde. In order to make the comparison good it was necessary to have definite yields from the benzaldehyde-amide condensation. While this condensation, using benzaldehyde and various amides, has been studied by a host of workers in the past sixty years, the study has been carried out under very different conditions and in many cases the yields are not to be found. In the present investigation, therefore, it was necessary to have the figures of the yields of the condensations of benzaldehyde with various amides employing the same method that might be used for the chloro-benzaldehydes. Some of these benzylidene-amides have been well known: others described here have been obtained for the first time.

Chlorine is found, on the whole, to increase the yield of the condensation product, though not in all cases. The conclusion has to be also limited by the fact that only the *o*-chlorobenzaldehyde has been studied here, the *m*- and the *p*- ones being not available at the moment.

In the condensations reported in the earlier eleven papers, it was found that heating the aldehyde and the amide alone together was one of the best of the processes: in some cases, however, the yields were distinctly improved by the use of 0·1–0·15 mol. of pyridine, though this was not so in all the cases examined. Here also pyridine has been found to improve the yield by 1 to 5%: but temperature and the time of heating had a more pronounced effect.

The products have generally been of the benzylidene-bisamide type, though, in the earlier papers, the monoamides too have been met with.[2] The aldol that must have presumably preceded the monoamide, has not so

far been obtained by any worker. Both benzaldehyde and *o*-chlorobenzaldehyde gave bisamide products. Formamide presented the usual difficulty, giving only a 13% yield with benzaldehyde. Another worker here (Mr. K. K. Baslas) had obtained a 36% yield in 1942.[3]

Experimental

Condensation of Benzaldehyde with Amides

With Benzamide.

Roth's[4] experiment as well as that of Hoffmann and Victor Meyer,[5] namely that of heating the aldehyde and the amide alone was first repeated.

i. *In the Absence of Pyridine or any Condensing Agent.*—0·5 g. benzaldehyde and 1·2 g. benzamide (1 : 2 mol.) were heated together in a 50 c.c. round-bottomed flask on a water-bath for six hours. The mixture first melted to a colourless liquid, which gradually passed on to a straw-yellow and a distinct yellow colour. Water vapours were seen coming out, there being no condenser. After two hours the colour was yellowish brown which became brown after four hours. After six hours' heating, the flask was left overnight. Next morning a dirty brown crystalline solid appeared, which was insoluble in water and in ether. The substance was taken out, crushed and shaken with 20 c.c. of hot water. The insoluble matter was removed by rapid filtration and washed again with hot water to remove all the remaining benzamide. It was washed with small quantities of ether to remove the unreacted aldehyde. The milky white needle-crystals were dried, and melted at 198°. The product was insoluble also in chloroform and benzene, sparingly soluble in methyl alcohol and acetone, and readily soluble in hot alcohol. It was recrystallised thrice from hot dilute alcohol, when the melting point remained stationary at 217·5° (Victor Meyer obtained 218° after recrystallising it four times[5]). The yield was 0·36 g. or 21·8% of theory.

ii. *In the Presence of Pyridine-Trace.*—The same amounts were taken with 0·05 c.c. of pyridine (1 : 2 : 0·1 mol.) and heated on water-bath for six hours as before. The observations and the procedure were the same. The purified product as well as the mixture of the products of the two experiments gave the same melting point. The yield was 0·39 g. or 23% of theory.

iii. Another experiment with 0·5 mol. of pyridine, *i.e.*, 0·25 c.c., but treated exactly as above, gave the same yield of 23%.

iv. With 0·1 mol. of pyridine, but on reducing the heating to only two hours on water-bath, the yield decreased to 0·2 g. or 12·4% of theory.

v. Taking again no pyridine but heating at 115° for six hours gave a hard dark brown product, which gave, on purification, a good melting point, weighed 1·05 g. and was thus 63·6% in yield. This was the best yield obtained.

vi. When the molecular proportions were 1: 1 and there was no pyridine, and the heating was carried out by the smallest flame with asbestos for two hours, the yield was only 8%.

(Found: N = 8·73%; benzylidene-bisbenzamide $C_{21}H_{18}O_2N_2$ requires 8·48%. The mono-amide would require 6·69%.) It gave no colour with concentrated sulphuric acid and did not decolorise Baeyer's reagent in the cold indicating an absence of unsaturation.

Condensation with Acetamide.

i. *In the Absence of any Condensing Agent.*—1·0 g. benzaldehyde and 1·2 g. acetamide (1:2) were heated as above on water-bath for six hours. A solid began to separate after 3 hours. Next day a yellow crystalline solid appeared in the cold flask. It was taken out and treated with water and ether as before. Silky white needle-crystals melting at 212° were obtained, which on recrystallisation (hot alcohol) finally melted at 245°. The yield was 0·35 g. or 17% of theory, calculated as bisamide. It has been prepared by Roth,[4] and recently by Noyes and Forman,[6] who refluxed the amide and the aldehyde with acetic acid for four hours and who report the melting-point as 238° and a 48% yield.

ii. *In the Presence of Pyridine-Trace.*—To the same quantities of the aldehyde and the amide, 0·1 c.c. of pyridine was added (1:2:0·1 mol.), and the whole heated as before on a water-bath for six hours. The product melted at 245° and the yield was 0·39 g. or 19·5°.

iii. *Heating Without any Condensing Agent for* 18 *Hours.*—The product was hard, brown and in an increased amount. Yield = 1·1 g. or 55% of theory.

iv. *Heating at Higher Temperatures.*—The heating was at 115° for six hours. The yield was 1·0 g. or 50% of theory. (Found: N = 13·84%; benzylidene-bisacetamide $C_{11}H_{14}O_2N_2$ requires 13·59%.) Its solubility and reactions were the same as those described for the bis-benzamide derivative.

Condensation with Formamide.

This has been studied by Bülow,[7] whose experiment was repeated.

i. *In the Absence of any Condensing Agent.*—1·0 g. of benzaldehyde and 0·9 g. of formamide were taken (1:2 mol.) and heated on a water-bath for 24 hours (in four days). Water vapour came out and the colour changed to pale yellow and then to orange-yellow. A sticky solid also made its

appearance, which after treatment with water and ether melted at 130°. On recrystallisation from hot alcohol it became a white crystalline material melting at 148° (Bülow gives 149–50° [7]). It was soluble in hot water and hot alcohol. The yield was only 0·15 g. or 9% of theory.

ii. *In the Presence of Pyridine-Trace.*—0·1 c.c. of pyridine was added to the same amounts and the mixture was heated on as before. The yield was slightly better, 13·2% of theory.

The product was soluble in hot water and hot alcohol, and gave no reaction with Baeyer's Reagent and with concentrated sulphuric acid, and was identical with Bülow's benzylidene-bisformamide.

iii. *At Higher Temperature.*—Following Bülow, the two were kept in a flask provided with a reflux condenser and heated with a small flame on asbestos wire-gauze, so that it kept on boiling very gently. In five minutes the liquid became pale yellow, yellow and lastly dark brown. The heating was stopped after two hours. The dirty yellow amorphous product, obtained after treatment with water and ether, melted at 240°, and after recrystallisation (alcohol), at 246°, corresponding to Bülow's 246–47°. It was tetraphenylpyrazine: the yield was only 18% of theory. It decolorised bromine water and alkaline permanganate in the cold and gave a brownish colour with concentrated sulphuric acid.

Condensation with Propionamide.

0·5 G. benzaldehyde and 0·7 g. propionamide were heated alone on a water-bath for three hours. Next morning a pale yellow solid appeared which did not melt on the water-bath. The flask was therefore put on an oil-bath and the bath gradually raised to 120° when the reactants again fused to a yellow liquid. The heating was continued for five hours more, when the product had a brown-yellow colour. The crystalline solid was treated with water and ether and became beautiful milk-white needle crystals, melting at 218°. Recrystallised (alcohol), the melting point rose very little, becoming 220°. (Found: N = 12·56%; the benzylidene-bispropionamide $C_{13}H_{18}N_2$ requires 11·97%.) The yield was 0·35 g. or 30·7% of theory. Its properties were similar to those of the other bisamides mentioned above.

Condensation with n-*Butyramide.*

0·5 G. benzaldehyde and 0·9 g. *n*-butyramide were heated on a water-bath. As only some of the amide dissolved by this time and as higher temperatures are favourable to better yields, the flask was transferred to an oil-bath at 110–15°, when complete fusion to a clear liquid took place. After

five hours the heating was stopped. Next morning plenty of aldehyde was found still left and so the temperature was raised to 115°. As all the substance did not fuse, the temperature was raised to 130° when a full melting occurred. The heating was carried on for three hours more. The brown solid product was extracted in the usual way. White needle-like crystals melting at 160° were obtained. Recrystallisation (alcohol) raised the melting point to 170°. It had the same properties as described above. (Found: N = 10·74%; benzylidene-bis-*n*-butyramide $C_{15}H_{22}O_2N_2$ requires 10·68%.) The yield was 1·1 g. or 86% of theory.

Condensation with n-*Heptamide.*

0·5 G. benzaldehyde and 1·3 g. *n*-heptamide (1 : 2 mol.) were heated as usual on water-bath for 5 hours. Next morning a yellow solid mass was seen which smelt distinctly of benzaldehyde and therefore the heating was continued, first on water-bath, later on an oil-bath at 120° when the reactants changed into a yellow liquid. After 2 hours' heating, the bath was raised to 130° and the heating continued for another four hours. The dirty brown mass was treated next morning with water and ether and gave a white crystalline product melting at 124°. Recrystallisation (alcohol) raised the meltingpoint to 128°. (Found: N = 7·92%; benzylidene-bis-*n*-heptamide $C_{21}H_{34}O_2N_2$ requires 8·09%.) The yield was 0·82 g. or 48·2% of theory. Its reactions were similar to those of the other bisamides above.

Condensation with Cinnamamide.

0·5 G. benzaldehyde and 1·47 g. cinnamamide (prepared in the laboratory from the acid) were heated on an oil-bath at 130°. After four hours in this way, the temperature was raised next day to 160° and the heating continued for 5 hours. Next morning the mass was found to be so hard that it could not be powdered with a glass rod. The usual treatment released a brownish powder melting at 216°. On recrystallisation the melting point rose to 238° and retained a buff colour. (Found: N = 7·26%; benzylidene-biscinnamamide requires 7·33%.) The yield was 1·5 g. or 80% of theory. It decolorised bromine water and Baeyer's reagent in the cold, on account of the unsaturation present in cinnamamide.

Condensation of o-*Chlorobenzaldehyde*

Condensation with Acetamide.

1·4 G. *o*-chlorobenzaldehyde and 1·2 g. acetamide were taken.

i. *In the Absence of any Condensing Agent.*—The two were heated on water-bath for 5 hours. A yellow and not a very hard crystalline mass

appeared in the flask next morning, melting at 240°. Recrystallisation (hot alcohol) raised the melting point to 250°. The yield was 0·95 g. or as bisamide 40% of theory.

ii. *In the Presence of Pyridine-Trace.*—0·1 c.c. of pyridine was added (1:2:0·1 mol.) to the same amount of the two, and the whole was heated for five hours on water-bath. The yellow crystalline product was next day treated as usual, when it gave white needles, melting at 240°, and, after purification at 250°. The yield was 1·05 g. or, as bisamide, 43·4% of theory.

iii. *Higher Temperature Without a Condensing Agent.*—The aldehyde and the amide were heated alone on an oil-bath at 110° for 5 hours. Next morning the brown product was treated as usual and was changed into white crystals melting at 241°, which on recrystallisation melted at 250°. The yield was 1·3 g. or 54·5% as bisamide. On fusion with sodium, the product showed that it contained chlorine. (Found: Cl = 14·33%; *o*-chlorobenzylidenebisacetamide $C_{11}H_{13}O_2N_2Cl$ requires 14·76%. The mono-amide would require 19·55%. (Found: N = 11·48%; the above bisacetamide requires 11·22%.) Its properties were similar to those of the corresponding benzylidene-bisacetamide.

Condensation with Propionamide.

o-Chlorobenzaldehyde 1·4 g. and propionamide 1·5 g. were taken.

i. *In the Absence of any Condensing Reagent.*—The two were heated alone on water-bath for 5 hours. Next day they had to be kept on an oil-bath at 115° to ensure fusion, the heating being for 5 hours. Brown hard crystalline mass soon changed to white crystals under the usual treatment, and melted at 210°, the recrystallised pure product melting at 216°. The yield was 1·8 g. or as bispropionamide 67% of theory.

ii. *In the Presence of Pyridine-Trace.*—The same amounts were heated with 0·1 c.c. of pyridine (1:2:0·1 mol.) on water-bath for 4 hours and, the next day, on an oil-bath at 115° for 5 hours. The product came out as usual, weighing 1·9 g. or as bisamide 68·3% of theory. The melting and the mixed melting points were identical, and so were its properties. (Found: Cl = 12·99%; *o*-chlorobenzylidenebispropionamide $C_{13}H_{17}O_2N_2Cl$ requires 13·22%.)

Condensation with n-*Butyramide.*

o-Chlorobenzaldehyde 1·4 g. and *n*-butyramide 1·75 g. (1:2 mol.) were taken.

i. *Heating alone at* 130°.—The two were heated on a water-bath for 4 hours on one day and the next day at 120° for another 2 hours and at

125-30° for 2 hours more. After purification the product melted at 173° and after recrystallisation the final melting point was 180°. The yield was 1·9 g. or 64·2% of theory.

ii. *Heating alone up to* 145°.—The heating was for 3 hours at 130° and for 3 hours at 140-45°. The product was 2·5 g. or 86% of theory. (Found: Cl = 11·64%; the *o*-chlorobenzylidene-bis-*n*-butyramide $C_{15}H_{21}O_2N_2Cl$ requires 11·97%.)

Condensation with Benzamide.

i. *In the Absence of any Condensing Agent.*—*o*-Chlorobenzaldehyde 1·4 g. and benzamide 2·4 g. were heated together first on water-bath and then on an oil-bath at 110° for about 4 hours in all. The next day the mixture was heated at 140° for 3 hours. The crude white crystals melted at 200°; recrystallised (dilute hot alcohol) the product melted at 215°. The yield was 2·5 g. or 70% of theory.

ii. *In the Presence of Pyridine-Trace.*—In the presence of 0·1 mol. of pyridine and heated at 110° for three hours and 140° for another three hours, the same product was obtained, melting at 215° after recrystallisations. The yield was 2·7 g. or 74·5% of theory. (Found: Cl = 9·39%; *o*-chlorobenzylidene-bisbenzamide $C_{21}H_{15}O_2N_2Cl$ requires 9·74%.)

Condensation with Formamide.

In the Absence of any Condensing Agent.—*o*-Chlorobenzaldehyde 1·4 g. and formamide 0·9 g. were heated alone. In one experiment, (i) on water-bath for 30 hours in 5 days. A brown sticky mass was obtained, which, by means of the usual process, gave a crude product melting at 169°. When recrystallised (alcohol), it finally melted at 176°. It was straw yellow in colour. The yield was only 8% of the theory, as bisamide. In the second experiment, (ii) the two were heated at 140° for five hours. Next morning a dark brown viscous liquid was left. It was washed with water. On treating it with ether, it was found to dissolve completely in it, leaving no insoluble solid. After the evaporation of ether, it was shaken up with a saturated solution of sodium bisulphite, when some solid derivative, possibly of the aldehyde, separated. But the residue remained a liquid from which no solid derivative could be isolated. It was obvious that the heating was insufficient.

The solid obtained in (i) gave on analysis Cl = 16·3%; *o*-chlorobenzylidenebisformamide $C_9H_9O_2N_2Cl$ requires 16·70%. Its properties were similar.

Condensation with n-Heptamide.

o-Chlorobenzaldehyde 1·4 g. and *n*-heptamide 2·6 g. (1 : 2 mol.) were heated on a water-bath for two hours, when a solid began to separate. The heating was continued at 110° for four hours; more solid separated in the beginning but later on it went into solution, thus at the end of the heating there was no solid in the flask. Next morning the solid that had come out was found to contain plenty of the free aldehyde, and so the heating was continued at 125° when the solid again went in solution. After 2 hours a solid again came out which increased in amount gradually, the heating being stopped after five hours. The hard brown crystalline product found next morning, gave after the usual treatment, a white crystalline product melting at 135°, and after recrystallisation, 141°. (Found: Cl = 9·09%; *o*-chlorobenzylidene-bis-*n*-heptamide $C_{21}H_{33}O_2N_2Cl$ requires 9·32%.) The yield was 3·1 g. or 81·6% of theory. Its properties were similar.

Condensation with Cinnamamide.

o-Chlorobenzaldehyde 1·4 g. and cinnamamide 2·9 g. were heated together (1 : 2 mol.) first on water-bath and then on an oil-bath at 120° when the reactants melted to a brown liquid. After 2 hours the temperature had to be raised to 130° for 2 hours and to 140° for another 2 hours. The next day the hard dark brown mass, on the usual treatment, gave a brown powder melting at 216° which, after several recrystallisations, melted finally at 232°. It was a buff coloured substance. (Found: Cl = 8·08%; *o*-chlorobenzylidenebiscinnamamide $C_{25}H_{21}O_2N_2Cl$ requires 8·52%.) The yield was 3 g. or 72% of theory. As before in the case of the benzaldehyde compound, it decolorised bromine water and Baeyer's reagent in the cold and gave a brown colour to concentrated sulphuric acid.

	Benzaldehyde		*o*-Chloro-benzaldehyde	
Amides	Maximum yield %	Melting point	Maximum yield %	Melting point
Formamide ..	13·2	148° C.	8	176° C.
Acetamide ..	55	245° C.	54·5	250° C.
Propionamide ..	30·7	220° C.	68	216° C.
n-Butyramide ..	86	170° C.	86	180° C.
n-Heptamide ..	48·2	128° C.	81·6	141° C.
Benzamide ..	63·6	217·5° C.	74·5	215° C.
Cinnamamide ..	80	238° C.	72	240° C.

SUMMARY

The condensation of benzaldehyde and of *o*-chlorobenzaldehyde with several amides has been studied, in the presence as well as in the absence of pyridine. The base slightly increased the yield in many cases. The rise of temperature as well as the prolongation of heating raised the yield more effectively. All the products were the corresponding bisamides. The presence of chlorine on the aromatic ring of the aldehyde, had the expected tendency to increase the yield, particularly in the condensations with benzamide, propionamide and *n*-heptamide. Condensations with formamide, as has been the general experience, did not give good yields; in all other cases, the yields were good, starting from 30% and reaching up to 86% in some cases.

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CHEMICAL EXAMINATION OF THE FIXED OIL DERIVED FROM THE WOOD OF *PTEROCARPUS MARSUPIUM* ROXB.—PART I

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Pterocarpus Marsupium Roxb., commonly known in Hindi and Bengali as 'Bija Sal', is a large deciduous tree, belonging to the Natural Order 'Papilionaceæ'. It grows all over India, especially in the extreme south-east corner of Kumaon, Oudh forest, Gorakhpur, Central and South India and as far as Rajmahal hills in Bihar and Ceylon.

The wood is heavy, close-grained, and yellowish-brown in colour with an aromatic smell. The heart-wood is darker than the sap-wood and often contains dark coloured streaks. The wood is very commonly used in making doorsills, doors and furniture in general as a cheap substitute for teak. Recently the Railway Board of India has been using it for sleepers with success in place of sal, because it is not affected by white-ants and other insects and does not undergo any fungous rot on storage.

According to Kirtikar and Basu[1] and K. L. Dey,[2] the wood has got interesting medicinal properties. On account of its bitter and astringent action it has been used for a long time in this country for the cure of diabetes. Generally, the patient is asked to have a cup made of the wood in which water is kept overnight and the decoction drunk next morning. This is repeated for a number of days, until the wood is exhausted, when it is thrown away and a fresh cup made. A paste made from the wood by rubbing it on a stone slab with water is used for sores, boils, etc. In the bark of this and other species of this genus are sacs filled with a red astringent oily gum, which is obtained by making incisions in the bark and sold as East Indian Kino. This Kino being an officinal is used as an astringent medicine in diarrhœa and pyrosis. Its action being milder, it is better adapted for children and delicate females.

The chemical constituents of the wood, which impart to it the medicinal properties described above, are not known, and the wood does not seem to have been chemically examined as yet. In the present investigation the

wood has been found to contain 0·52% of a fixed oil, potassium nitrate, an essential oil and 0·25% of a fine yellow colouring matter and one should not be surprised if these products are responsible for its medicinal properties. In this paper, the fixed oil obtained from the petroleum ether extract of the wood shavings has been examined.

A detailed examination of the oil has shown that the component liquid acids are oleic 41·59%, linoleic 35·91% and linolenic 3·38%. A special feature of the oil is that it contains a high percentage of the unsaponifiable matter and a low percentage of solid fatty acids. The solid fatty acids have been obtained in insufficient amount for a thorough quantitative examination. The unsaponifiable matter will be dealt in Part II of this series.

Experimental

A big lot of the authentic specimen of wood was chipped, dried in sunlight and beaten into small shavings. In order to have an approximate idea regarding the solubility of the constituents of wood in different solvents, the coarsely powdered shavings were extracted in lots of 200 gm. with a number of solvents and after filtration the solvent was evaporated in each case and the residue brought to a constant weight by keeping in a steam oven. The following results were obtained.

Petroleum-ether extract (0·59%).—A sweet smelling yellow oily liquid, turning yellow with caustic soda solution and reddish yellow with strong sulphuric acid.

Benzene extract (1·5%).—A yellow oily liquid soluble in hot alcoholic caustic potash solution.

Chloroform-extract (4·41%).—A reddish yellow oily substance, slightly soluble in alcohol and insoluble in water, but developing a yellow colour with caustic soda solution.

Ether extract (2·14%).—A yellow fatty and resinous substance, soluble in alcohol, yellow with caustic soda and red with strong sulphuric acid.

Ethyl acetate extract (11·01%).—A brown resinous substance, acidic to litmus, soluble in water, yellow with caustic soda, dark red with strong sulphuric acid and finally decolourising bromine water.

Alcohol extract (19·92%).—A dark brown solid, slightly acidic, soluble in water and also in caustic soda, giving a red colour with strong sulphuric acid, an orange precipitate with lead acetate and reducing Fehling's solution.

Aqueous extract (16·78%).—A brown substance soluble in caustic soda solution and giving a red colouration with ferric chloride.

For complete extraction about 15 kilos of small shavings were extracted with petroleum ether (b.p. 40–60° C.) in a five litre extraction flask. On distilling off the solvent about 80 gm. of a reddish brown oil having a characteristic smell were obtained. The oil was allowed to stand overnight but nothing was deposited. It was subjected to steam distillation, whereby the volatile oil was removed. Now there remained in the distilling flask an aqueous layer and above it an oily layer. The oily layer was separated by means of a separating funnel and dissolved in petroleum-ether. The aqueous layer was discarded. On distilling off the solvent, a dark red oil was obtained and was purified with animal charcoal and fuller's earth, having the following physical and chemical constants as recorded in Table I. The yield of the oil was 0·52% on the weight of wood shavings.

The shavings after complete extraction with petroleum-ether were further extracted with alcohol. The examination of the alcoholic extract containing the colouring matter will be the subject of communication in the next paper.

TABLE I

Specific gravity $\frac{\text{Oil } 25°\text{C.}}{\text{Water } 25°\text{C.}}$	..	0·9082
Refractive index ($n_d^{28°\text{C.}}$)	..	1·4648
Acid value	..	18·68
Saponification value	..	189·9
Acetyl value	..	40·5
Iodine value (Wijs)	..	105·8
Hehner value	..	94·4
Unsaponifiable matter	..	7·5%

60 gm. of the oil were saponified with 20% alcoholic caustic potash and the unsaponifiable matter extracted with ether as usual. The ethereal solution was set aside and examined in Part II of this series. The soap was then dissolved in hot water, the solution cooled and decomposed with dilute hydrochloric acid in presence of ether. The ethereal solution of the fatty acids was freed from the solvent by distillation. The fatty acids thus obtained had the following physical and chemical constants as recorded in Table II.

TABLE II

Consistency	..	Liquid
Neutralisation value	..	200·4
Saponification value	..	200·3
Mean molecular weight	..	280·1
Iodine value (Wijs)	..	117·8

The mixture of fatty acids described above was then separated into solid and liquid acids by Twitchell's[3] lead salt alcohol process. The solid

acids were obtained in small quantities only and were insufficient for thorough quantitative examination. Hence the solid acids were examined qualitatively and the liquid acids quantitatively. The following table gives the percentage, iodine value (Wijs) and neutralisation value of the solid and liquid acids (Table III).

TABLE III

Examination of the Liquid Acids

Acids	Percentage in oil	Percentage in mixed acids	I.V.	N.V.
Solid ..	6·12	7·03	0·64	202·3
Liquid ..	80·88	92·96	137·7	198·9

EXAMINATION OF THE LIQUID ACIDS

Oxidation with Potassium Permanganate.—The liquid acids on oxidation according to the method of Lapworth and Mottram[4] gave a dihydroxy stearic acid, m.p. 130° C., a tetrahydroxy stearic acid, m.p. 172° C., and a hexahydroxy stearic acid, m.p. 202° C., showing the presence of oleic, linoleic and linolenic acids.

Bromination Method.—The constituents of the liquid acids were determined quantitatively according to the method of Eibner and Muggenthaler[5] modified by Jamieson and Baughman,[6] whereby the bromine addition products of the constituent acids were prepared at — 10° C. and examined. Linolenic hexabromide, m.p. 180–81° C., and linoleic tetrabromide, m.p. 113° C., were confirmed when their melting points on admixture with pure samples of linolenic hexabromide and linoleic tetrabromide respectively remained undepressed. The results are given in Table IV.

TABLE IV

Weight of liquid acids taken ..	5·2738	gm.
Weight of linolenic hexabromide ..	0·6008	,,
Percentage of bromine in the above (Piria and Schiff's) method ..	62·88	
Weight of linolenic acid ..	0·2204	,,
Weight of linoleic tetrabromide ..	3·9964	,,
Percentage of bromine ..	53·08	
Weight of linoleic acid ..	1·8650	,,
Weight of the residue (di- and tetrabromides) ..	5·2716	,,
Percentage of bromine ..	39·51	
Weight of oleic acid ..	2·7117	,,
Total weight of linoleic acid ..	2·3415	,,

The percentage of the various acids in liquid acids, mixed acids and the oil is given in Table V.

TABLE V

Examination of the Solid Acids

Acids		Percentage in liquid acids	Percentage in mixed acids	Percentage in oil
Oleic	..	51·42	47·80	41·59
Linoleic	..	44·40	41·28	35·91
Linolenic	..	4·18	3·88	3·38

EXAMINATION OF THE SOLID ACIDS

As the solid acids were obtained in insufficient amounts for a thorough quantitative examination, these were examined qualitatively only. The crude acids melted at 57° C. On repeated crystallisation from acetone two fractions were obtained, one melting at 67–68° C. and another at 61° C. The melting points of both the fractions on admixture with pure samples of stearic acid and palmitic acid respectively remained unchanged. Thus stearic and palmitic acids were confirmed in the solid acids.

SUMMARY

The wood shavings of *Pterocarpus Marsupium* on extraction with petroleum-ether (b.p. 40–60° C.) have been found to yield 0·52% of a semi-drying oil having $d^{25°}$ 0·9082, $n_d^{25°\,C.}$ 1·4648, acid value 18·68, sap. value 189·9, acetyl value 40·5, Hehner value 94·4, iodine value (Wijs) 105·8 and unsaponifiable matter 7·5%.

The component liquid acids on further examination have been found to give linolenic 3·38%, linoleic 35·91% and oleic 41·59%.

The solid fatty acids being insufficient for a thorough quantitative examination, have been examined qualitatively only and are found to yield palmitic and stearic acids.

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CHEMICAL EXAMINATION OF THE FIXED OIL DERIVED FROM THE WOOD OF *PTEROCARPUS MARSUPIUM* ROXB.

Part II. Isolation of Pterocarpol A and Pterocarpol B

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IN the previous paper on this subject the author, in course of his investigation on the chemical constituents of the fixed oil, has referred to the ethereal solution of the unsaponifiable matter. From this ethereal solution two compounds of the nature of phytosterols (*a*) m.p. 112° C. and (*b*) m.p. 161° C. have been obtained after purification according to the method of Windaus and Hauth.[1] These have been named Pterocarpol A and Pterocarpol B respectively. In the present paper, the isolation as well as the systematic chemical examination of both the sterols is recorded.

A detailed examination of pterocarpol A, $C_{27}H_{46}O$. $2H_2O$ after drying in air and $C_{27}H_{46}O$ after drying at 100° C. *in vacuo*, has shown only one hydroxy group in the molecule and it gives reactions of a phytosterol. The compound pterocarpol B, $C_{27}H_{46}O$ after drying at 110° C. *in vacuo* has been also found to contain one hydroxy group in the molecule and to give the reactions of a phytosterol. Thus pterocarpol A and pterocarpol B are obtained in an yield of 0·011% and 0·005% respectively on the weight of wood shavings.

EXPERIMENTAL

Isolation of pterocarpol A and pterocarpol B.—The ethereal solution of the unsaponifiable matter as described in Part I, was now distilled to recover the solvent completely. The residue was treated with benzene in which it was only partially soluble. The insoluble product was filtered and the filtrate was distilled to recover benzene. The residue after distilling benzene was repeatedly crystallised from methyl alcohol with the addition of animal charcoal in white flakes, m.p. 110° C. (Fraction I).

The benzene-insoluble product was then dissolved in chloroform. The greater part of the solvent was distilled off and the concentrated solution allowed to stand overnight, but nothing crystallised out. Hence the solvent

was completely evaporated off and the residue crystallised from methyl alcohol a number of times with the addition of animal charcoal until colourless leaflets, m.p. 158° C., were obtained (Fraction II). Both the fractions were further purified according to the method of Windaus and Hauth (*loc. cit.*).

The Fraction I (3 gm.) was acetylated as usual and crystallised from alcohol in colourless needles, m.p. 92° C. This acetyl derivative was dissolved in ether (25 c.c.) and treated with a 5% solution of bromine in glacial acetic acid (35 c.c.). The brown solution was allowed to stand overnight in a frigidaire, when a yellowish precipitate was obtained. This precipitate was filtered, washed with 75% acetic acid and dried in a vacuum over strong sulphuric acid. The dried product was crystallised from chloroform in yellow leaflets, m.p. 86° C. It was debrominated by boiling with zinc dust (2 gm.), glacial acetic acid (5 c.c.) and alcohol (40 c.c.) for three hours. The colourless solution was filtered to remove the excess of zinc, diluted with water and extracted with ether. The ethereal solution was evaporated and the residue saponified by boiling with alcoholic caustic potash. The solution was diluted with water, the residue extracted with ether and the solvent was evaporated off. The remaining residue on crystallisation from methyl alcohol gave colourless leaflets, m.p. 112° C. The yield of pterocarpol A thus obtained was 1·3 gm., *i.e.*, 0·011% on the weight of wood shavings.

The Fraction II (1·3 gm.) was acetylated, brominated and debrominated in order to get the pure sterol similarly as Fraction I. The acetyl derivative was obtained in white flakes, m.p. 120° C. The brominated product, acetyl pterocarpol B dibromide on crystallisation from chloroform gave yellow needles, m.p. 111° C. The debrominated product was saponified by boiling with alcoholic caustic potash, diluted with water and the residue extracted with ether. From this ethereal solution, the solvent was evaporated off and the remaining residue crystallised from anhydrous ether in white flakes, m.p. 161° C. The flakes were dried at 110° C. *in vacuo* and the melting point determined but it remained unchanged. Thus the yield of pterocarpol B was 0·58 gm., *i.e.*, 0·005% on the weight of wood shavings.

Pterocarpol A.—It crystallises from methyl alcohol in colourless leaflets. It is soluble in benzene, chloroform and ether, sparingly soluble in methyl alcohol and ethyl alcohol and insoluble in petroleum-ether and water. In strong sulphuric acid, it dissolves with a yellow colour, which turns intense red on warming the solution. From this solution it recovers unchanged on dilution with water like alangol.[2] It gives a positive Liebermann-Burchard's[3] test showing red, violet, blue and green colour. In Salkowski's[4] reaction, it assumes a brown colouration which turns green. It is optically active

having in chloroform a lævorotation of $[\alpha]_d^{20°\,C.} = -27·7°$. [Found in air-dried sample: C = 76·63; H = 11·98; loss (H_2O) on drying = 8·45; M.W. by Rast's camphor method = 418, 425; $C_{27}H_{46}O.\ 2H_2O$ requires C = 76·78; H = 11·85; loss (H_2O) on drying = 8·53%; M.W. = 422. Found in the sample dried at 110° C. *in vacuo*: C = 83·79; H = 12·04; M.W. by Rast's camphor method = 385, 390; $C_{27}H_{46}O$ requires C = 83·92; H = 11·92%; M.W. = 386.]

Monoacetyl Pterocarpol A.—It was prepared by heating the substance (0·25 gm.) with acetic anhydride (10 c.c.) and pyridine (3 c.c.) under reflux on a water-bath for an hour. The mixture was poured into water and kept overnight when a precipitate was obtained. It was filtered, washed with water and crystallised from alcohol in colourless needles, m.p. 92° C. The yield was 74·8% of the theoretical. (Found: C = 81·16; H = 11·34; $C_{27}H_{45}O.\ CO.CH_3$ requires C = 81·32; H = 11·21%.)

Monobenzoyl Pterocarpol A.—The substance (0·2 gm.), benzoyl chloride (5 c.c.) and pyridine (10 c.c.) were heated under reflux on a water-bath for an hour. The product was poured into water and kept overnight. On the next day a white precipitate was obtained. It was filtered, washed with water and crystallised from alcohol in colourless prisms. The yield of this derivative, m.p. 95° C., was 91·2% of the theoretical. (Found: C = 83·12; H = 10·32; $C_{27}H_{45}O.\ CO.C_6H_5$ requires C = 83·28; H = 10·21%.)

Monoacetyl Pterocarpol A Dibromide.—Monoacetyl pterocarpol A (0·1 gm.) was dissolved in ether (5 c.c.) and treated with a 5% solution of bromine in glacial acetic acid (10 c.c.). The brown solution was allowed to stand overnight in a frigidaire, when a yellowish precipitate was obtained. This precipitate was filtered, washed with 75% acetic acid and dried in a vacuum over strong sulphuric acid. The dried product on crystallisation from chloroform gave yellow leaflets, m.p. 86° C. The yield was 0·1368 gm. (Found: Br = 26·89; $C_{29}H_{48}O_2Br_2$ requires Br = 27·2%.)

Pterocarpol A Monophenylurethane.—This was prepared by allowing a mixture of the substance (0·2 gm.), phenylisocyanate (1 gm.) and dry benzene (30 c.c.) to stand at the ordinary temperature in a stoppered flask for three days, when from the clear solution, some of the phenylurethane derivative crystallised out. More of the substance was obtained by distilling off greater part of the solvent and allowing the concentrate to crystallise for two days. The combined product was recrystallised from boiling alcohol in colourless prisms), m.p. 102° C. It was obtained in an yield of 61·2% of the theoretical. (Found: N = 2·69; $C_{27}H_{45}O.CO.NHC_6H_5$ requires N = 2·77%.)

Pterocarpol A Digitonide.—The substance (0·1 gm.) and digitonin (0·1 gm.) dissolved in alcohol (20 c.c.) were heated under reflux on a water-bath for two hours. On cooling the digitonide crystallised out in colourless leaflets, m.p. 188° C. and was thus obtained in practically quantitative yield of the theoretical. (Found: C = 61·39; H = 8·56; $C_{27}H_{46}O$. $C_{55}H_{90}O_{29}$ requires C = 61·51; H = 8·5%.)

Pterocarpol B.—It crystallises from ether in colourless glistening flakes. It is soluble in chloroform and pyridine, sparingly soluble in methyl alcohol and ethyl alcohol but insoluble in benzene and petroleum-ether. It gives a red coloration with strong sulphuric acid. With Liebermann-Burchard's test (*loc. cit.*), it gives pink, brown, violet and blue coloration. In Salkowski's reaction (*loc. cit.*), it gives a purple coloration which turns green finally. It gives a monoacetyl, a monoacetyl dibromide and a digitonide derivative, indicating the presence of an alcoholic hydroxy group in the molecule. (Found: C = 83·74; H = 12·1; M.W. by Rast's camphor method = 390, 392; $C_{27}H_{46}O$ requires C = 83·92; H = 11·92%; M.W. = 386.)

Monoacetyl Pterocarpol B.—The substance (0·2 gm.), acetic anhydride (10 c.c.) and pyridine (2 c.c.) were heated under reflux on a water-bath for 45 minutes and poured into water. On keeping overnight, a white precipitate was obtained. It was filtered, washed with water and crystallised from alcohol in colourless flakes, m.p. 120° C. The yield was 75·7% of the theoretical. (Found: C = 81·18; H = 11·32; $C_{27}H_{45}O.CO.CH_3$ requires C = 81·32; H = 11·21%.)

Monoacetyl Pterocarpol B Dibromide.—Monoacetyl pterocarpol B (0·12 gm.) was dissolved in ether (5 c.c.) and treated with a 5% solution of bromine in glacial acetic acid (10 c.c.) in small quantities at a time, until the solution was brown. This solution was kept overnight in a frigidaire. On the next day, a brown precipitate was obtained. It was filtered, washed with 75% acetic acid and dried in a vacuum over strong sulphuric acid. The dried product on crystallisation from chloroform gave yellow needles, m.p. 111° C. The yield was 0·1642 gm. (Found: Br = 26·94; $C_{29}H_{48}O_2Br_2$ requires Br = 27·2%.)

Pterocarpol B Digitonide.—This was prepared by heating under reflux a mixture of the substance (0·1 gm.) and digitonin (0·1 gm.) dissolved in alcohol (20 c.c.) for three hours. On cooling the digitonide crystallised out in colourless flakes, m.p. 215° C. The yield was practically quantitative of the theoretical. (Found: C = 61·40; H = 8·54; $C_{27}H_{46}O$. $C_{55}H_{90}O_{29}$ requires C = 61·51; H = 8·5%.)

Summary

From the unsaponifiable matter of the fixed oil of the wood of *Pterocarpus marsupium*, two phytosterols have been obtained. One of these has been named 'pterocarpol A', having a molecular formula $C_{27}H_{46}O.2H_2O$ after drying in air and $C_{27}H_{46}O$ after drying at 100° C. *in vacuo*. The other phytosterol has been named 'pterocarpol B', having a molecular formula $C_{27}H_{46}O$ after drying at 110° C. *in vacuo*.

Both have been found to contain an alcoholic hydroxy group as these give monoacetyl derivatives. Further pterocarpol A gives a monobenzoyl, a monoacetyl dibromide, a monophenylurethane and a digitonide derivative. Monoacetyl dibromide and digitonide derivatives of pterocarpol B have been also obtained.

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CHEMICAL EXAMINATION OF THE UNSAPONIFIABLE MATTER OF THE FAT FROM THE FLESHY ARILS OF *CELASTRUS PANICULATA*

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Celastrus paniculata commonly known as 'Malkangini' in Hindi and Bengali is a shrub belonging to the Natural order 'Celastraceæ'. It is cultivated in many parts of India, as far as Ceylon from the hilly districts of the Himalayas. The seeds are of the size of a millet, of reddish brown colour, oily and angular like the section of a sphere and are covered by the arils on the surface.

According to Dymock, Warden and Hooper[1] and Kirtikar and Basu[2] the seeds have been described to be highly medicinal in the indigenous system of medicine. Gunde and Hilditch[3] have examined the fat obtained from the husk or the arils of the seeds in detail, but not the unsaponifiable matter. Warsi,[4] however, claims to have isolated a sterol, m.p. 184° C. from the unsaponifiable matter but he has also not examined it further. In the present paper, therefore, the author has confirmed the nature of the unsaponifiable matter from which a sterol, namely 'Celastrol' and a resinous colouring matter have been isolated.

The arils on extraction with petroleum-ether (b.p. 40–60° C.) gave an orange red semi-solid fat. The fat on saponification, as usual, and extraction with ether gave an unsaponifiable matter 6·46% from which a phytosterol has been isolated according to the method of Windaus and Hauth.[5] In addition to this a highly coloured resinous product is also present in the crude unsaponifiable matter but could not be isolated in a pure form for examination.

The phytosterol 'Celastrol' ($C_{27}H_{46}O_3$), m.p. 142° C., is quite different from that detected by Warsi (*loc. cit.*). A number of derivatives of Celastrol have been prepared, which account for only one hydroxy group in the sterol. The nature of the remaining oxygen atoms is not yet known.

Experimental

About 10 kilos of the authentic specimen of the seeds together with the orange red arils were obtained from the Punjab Ayurvedic Pharmacy, Amritsar. The arils were separated very carefully from the seeds by the hand-picking method, thus giving an yield of 25% on the weight of seeds. These arils were completely extracted with petroleum-ether (b.p. 40–60°), when an orange red semi-solid fat was obtained. On purification with fuller's earth and animal-charcoal, it was obtained in an yield of 30% on the weight of arils.

450 gm. of the fat were saponified in the usual manner with 20% alcoholic caustic soda and the unsaponifiable matter extracted with ether. This ethereal solution was washed with water, dehydrated with anhydrous sodium sulphate, filtered and distilled to recover the solvent. The residue on repeated crystallisation from methyl alcohol with the addition of animal-charcoal gave white flakes, m.p. 141–42° C., but a part of it still remained resinous. This resinous residue was highly coloured and probably consisted of the colouring matter. It was dissolved in chloroform and precipitated with acetone. The precipitate was filtered and crystallised from methyl alcohol with the addition of animal-charcoal in white flakes, m.p. 141–42° C. These flakes were further purified by the method of Windaus and Hauth (*loc. cit.*).

The chloroform acetone solution was distilled to recover the solvent, when an orange red resinous residue was obtained. On crystallisation from methyl alcohol, two fractions were obtained but none of these could be isolated in a pure form.

The flakes obtained above were acetylated as usual and crystallised from methyl alcohol in colourless leaflets, m.p. 160° C. The acetylated product was dissolved in ether (30 c.c.) and treated with a 5% solution of bromine in glacial acetic acid (40 c.c.). The solution was brown indicating an excess of bromine. On keeping over night in a frigidaire, a white amorphous precipitate was obtained. It was filtered, washed with 75% acetic acid and dried in a vacuum over sulphuric acid. The acetyl-sterol dibromide formed a yellowish amorphous powder and was crystallised from chloroform in yellowish flakes, m.p. 81° C. It was debrominated by boiling with zinc dust (3 gm.), glacial acetic acid (10 c.c.) and alcohol (50 c.c.) for three hours. The colourless solution was filtered to remove the excess of zinc, diluted with water and extracted with ether. From the ethereal solution the solvent was evaporated and the residue saponified with alcoholic caustic potash. The solution was then diluted with water, the residue extracted with ether

and the solvent evaporated, when it gave a white product, which on crystallisation from methyl alcohol gave white flakes, m.p. 142° C. The yield of the product was 2·25 gm., thus giving an yield of 0·15% on the weight of arils. It has been named 'Celastrol'.

Properties.—Celastrol is a white crystalline substance, m.p. 142° C. It is soluble in petroleum-ether and chloroform, sparingly soluble in ethyl alcohol and methyl alcohol and insoluble in water. It remains insoluble in aqueous caustic potash and does not give any colouration with ferric chloride. In concentrated sulphuric acid, it gives a dark red colour. It assumes a red colouration in Salkowski's[6] reaction and ultimately turns green. With Liebermann-Burchard's[7] test, it turns yellow, red, brown, green and violet. Thus it gives reactions of a sterol.

It gives a monoacetyl and an acetyl dibromide derivative and forms a crystalline digitonide. [Found in air-dried sample: C = 71·18; H = 11·12; loss (H_2O) on drying = 8·05; M.W. by Rast's camphor method = 432, 470; $C_{27}H_{46}O_3 . 2H_2O$ requires C = 71·36; H = 11·01; loss (H_2O) on drying = 7·92%; M.W. = 454. Found in the sample dried at 110° C. *in vacuo*: C = 77·39; H = 11·10; M.W. = 410, 431; $C_{27}H_{46}O_3$ requires C = 77·50; H = 11·01%; M.W. = 418.]

Monoacetyl Celastrol.—Celastrol (2 gm.) was dissolved in pyridine (15 c.c.) and treated with acetic anhydride (40 c.c.). It was refluxed for half an hour on a water-bath, poured into cold water and kept overnight, when a precipitate was obtained. This precipitate was filtered, washed with water and crystallised from alcohol in colourless silky leaflets, m.p. 160° C. The yield was 78·7% of the theoretical. (Found: C = 75·47; H = 10·56; $C_{29}H_{48}O_4$ requires C = 75·65; H = 10·43%.)

Monoacetyl Celastrol Dibromide.—Monoacetyl celastrol (1·8 gm.) was dissolved in ether (20 c.c.) and treated with a 5% solution of bromine in glacial acetic acid (30 c.c.) in small quantities at a time, until the solution was brown. This solution was allowed to stand overnight in a frigidaire, when a yellowish amorphous precipitate was obtained. It was filtered, washed with 75% acetic acid and dried in a vacuum over strong sulphuric acid. This product on crystallisation from chloroform gave yellowish flakes, m.p. 81° C. The yield was 2·4182 gm. (Found: Br = 25·47; $C_{29}H_{48}O_4Br_2$ requires Br = 25·8%.)

Celastrol Digitonide.—This was prepared by heating under reflux a mixture of celastrol (0·2 gm.) and digitonin (0·2 gm.) dissolved in alcohol (60 c.c.) for three hours. On cooling the digitonide crystallised out in

colourless prisms, m.p. 195° C. The yield was practically theoretical. (Found: C = 60·20; H = 8·39; $C_{27}H_{46}O_3$. $C_{55}H_{90}O_{29}$ requires C = 60·3; H = 8·33%.)

Summary

The arils of *Celastrus paniculata* on examination have been found to give a semi-solid fat (30%), a phytosterol namely celastrol (0·15%) and a highly coloured resinous substance.

Celastrol obtained from the unsaponifiable matter has a molecular formula $C_{27}H_{46}O_3$. It contains an alcoholic hydroxy group and gives a monoacetyl, a monoacetyl dibromide and a digitonide derivative. The nature of the remaining oxygen atoms has not yet been known.

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OVERTONE AND COMBINATION LINES IN THE RAMAN SPECTRUM OF CHLOROFORM

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1. Introduction

In addition to the usual lines due to the fundamental frequencies of vibration in a Raman spectrum, there are also occasionally present overtone and combination tones. According to the theory of Placzek, developed on the assumption that the polarisability can be expanded in the form of a series, the overtone lines will be either of zero or negligibly small intensity, according as the second order derivative of polarisability is zero or negligibly small. Later, Bhagavantam has shown that the anharmonic nature of an oscillation may also contribute to the intensity of its overtone in Raman scattering.

Thus, overtones and combination tones are, in general, much weaker than the fundamentals. They may yet be observed in Raman effect by using sufficiently long exposure times. It is easier to get them in infra-red absorption and using sufficiently thick absorbing layers, several instances have been recorded. Liquid chloroform is studied in this paper with a view to record combination and overtone Raman lines using a sufficiently big tube to increase the illuminated volume of the liquid and giving lengthy exposures.

2. Experimental Arrangement

Chloroform was distilled repeatedly four or five times at constant temperature, discarding the first and last portions of the distillate each time. The pure liquid thus obtained is introduced into a thoroughly cleaned and dried dust-free Raman tube suitably painted with black paint. The condenser arrangement was used to photograph the scattered spectrum. The time of exposure was about hundred hours, and very intense pictures were recorded. Five combination and overtone lines are seen in the Raman spectrum.

3. Results

The Raman frequencies obtained by the author by taking the averages of measurements on four spectrograms are given in Table I along with those recorded by some earlier investigators. The six well-known frequencies

printed in bold type represent the fundamental vibrations. In addition, there are five others which have to be explained as first overtones or binary combinations of fundamentals.

TABLE I

Raman Frequencies of Chloroform

Ganesan[1] and Venkateswaran	Langer and Meggers[2]	Dabadghao[3]	Author	Assignment
261	**261**	**262**	**259**	Fundamental
368	**367**	**366**	**367**	,,
..	..	..	497	$757-259=493$ (E_2-E_2)
..	..	..	622	$259+364=623$ (E_2-A_1)
669	**668**	**667**	**664**	Fundamental
762	**760**	**762**	**757**	,,
..	..	..	1027	$757+259=1016$ (E_2+E_2)
1218	**1215**	**1213**	**1215**	Fundamental
1441	..	**1441**	1420	$757+664=1421$ (E_2+A_1)
..	..	..	1510	$757+757=1514$ $(2E_2)$
3019	**3019**	**3017**	**3018**	Fundamental
..	..	**3072**	..	..

The frequency at 3072 reported by Dabadghao is not confirmed by other workers. $\Delta\nu$ 1510 cm.$^{-1}$ appears to have been reported by some previous workers and assigned to be the first overtone of the fundamental at $\Delta\nu$ 757 cm^{-1} as there is a reference to it in Herzberg's book.[4]

4. DISCUSSION

The six fundamental frequencies recorded are to be expected from the assumed pyramidal structure (symmetry group C_{3v}) for the molecule of chloroform. The selection rules for the occurrence of overtones and combination tones in Raman effect have been obtained by Tisza.[5] The results for chloroform are worked out and presented in Table II.

TABLE II

	A_1	A_2	E_2
A_1 ..	A_1	A_2	E_2
A_2 ..		A_1	E_2
E_2 ..			$A_1+A_2+E_2$

Since A_1 and E_2 are allowed and A_2 is not allowed in Raman effect as fundamentals, all the combinations except $(A_1 + A_2)$ are allowed. $E_2 + E_2$ is also allowed because in the term $A_1 + A_2 + E_2$, A_1 and E_2 are active.

When the selection rules are applied to a difference band, one finds easily that it is allowed or forbidden depending on whether the corresponding summation band is allowed or forbidden. The intensity of a difference band would be expected to be much smaller than that of the corresponding summation, since the number of molecules in the initial state is much smaller, and the ratio will be governed by the Boltzmann factor. Therefore, a difference band cannot be expected to appear unless the corresponding summation band makes its appearance with a greater intensity. It can be seen from Table I, where the assignment of the various Raman shifts are given, that for the difference line recorded, the corresponding summation is also recorded and it is visually observed that the latter is more intense than the former. Quantitative work on the relative intensities of the difference and summation tones will be taken up in due course. It may be mentioned here that the value of the Boltzmann factor gets smaller and smaller for higher values of the frequencies, and hence, for taking up the problem of quantitative determination of the relative intensities of summation and difference lines, liquids having low fundamental frequencies (combinations between the fundamentals being allowed) have to be specially chosen.

The possibility that the additional lines may be due to their presence in the incident exciting radiation (here, a quartz mercury arc) or to the presence of slight traces of impurities in the liquid has to be examined. The spectrum of the mercury arc is separately photographed on the same plate on which the Raman spectrum is recorded, and it is seen that there are no lines in the region of the new Raman lines. Possible impurities in chloroform are, ethyl alcohol, phosgene in solution and acetone. The strong Raman lines due to each of these are given below:

Ethyl alcohol: $\Delta\nu$ 1051, 1455, 2878, 2928 and 2972 cm.$^{-1}$

Acetone: $\Delta\nu$ 532, 788, 1425, 1708, 2922, 2965 and 3005 cm.$^{-1}$

Phosgene (liquid): $\Delta\nu$ 301, 444, 571 and 1810 cm.$^{-1}$

None of these lines coincide with the new combination lines that are recorded.

5. Summary

An intense Raman spectrum of liquid chloroform has been obtained with a Fuess glass spectrograph. Besides the six fundamentals, five lines are recorded, which are to be explained as either combination tones or overtones. Of these five, two summation bands and one difference band are recorded for the first time. Taking into consideration the selection rules for the appearance of combination tones, a table is worked and it is found that all the combination tones recorded here are allowed.

In conclusion, the author takes this opportunity of expressing his grateful thanks to Prof. S. Bhagavantam, under whose direction this work was carried out.

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PRODUCTION OF *JOSHI-EFFECT* UNDER *UNI-*, AND *BI-*ELECTRODE EXCITATION

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The dependence[1, 2] of the magnitude of the above phenomenon $\triangle i$ on factors such as the gas pressure, nature of the solid-gas interface and electrical quantities, *e.g.*, the inter-electrode capacitance, wave-form and current frequency, etc., has been emphasised by Prof. Joshi. This is observed in a striking manner in the above modes of excitation, which have besides the advantage of keeping (most) other factors unaltered.

2. Fig. 1 shows the general circuit and apparatus used. It consisted essentially of a Siemens' ozoniser filled with purified chlorine at about 300 mm.

Fig 1. Joshi-Effect in Uni-, Bi-electrode Excitation

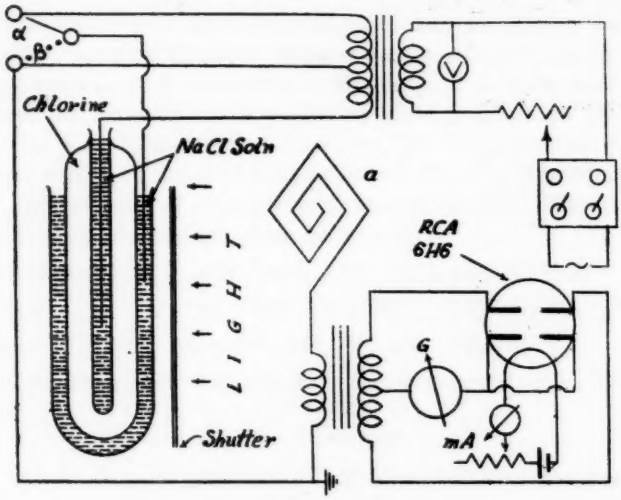

FIG. 1

pressure and excited in the range 5–9 kV of 50 cycles frequency; a frame aerial (*a*) and a double diode 6H6 (RCA). The two plates of the latter were connected to the secondaries of a Bell transformer; the aerial was connected in its primary. The cathodes were connected together and to the centre of

the secondary through a reflection galvanometer. The current i was observed in dark (i_d) and when the excited ozoniser was irradiated from an incandescent 200 watt, 220 volt (glass) bulb (i_l), under the following conditions, α and β:

(α) The inner and outer electrodes of the ozoniser were connected to the secondaries of an H.T. transformer, and whose centre was earthed (*vide* α, Fig. 1).

(β) The outer electrode of the ozoniser was earthed; the corresponding secondary terminal in (α) was left unconnected. Since only half of the transformer now comes into operation, the voltage applied to the ozoniser was maintained similar to that in (α) by adjustment of the primary potential. These connections are shown by (β) in Fig. 1. In the latter arrangement, *i.e.*, β, the potential of the inner electrode alternates between $+V$ and $-V$; the other electrode is throughout at zero potential. In (α) i is due to anti-phase excitation of the two electrodes. The results for only one typical series under (α) and (β) for the net *Joshi-effect* $i_d - i_l = \Delta i$, and its relative value $100 \times \frac{\Delta i}{i_d} = \% \Delta i$ are returned in Table I.

TABLE I

Potential-Variation of Joshi-Effect *under* Uni-, *and* Bi-*Electrode Excitation*

kV	i_{dark}	i_{light}	Δi	$\% \Delta i$
		Bi-electrode (α)		
5·3	1·4	1·3	0·1	7·1
5·6	1·6	1·4	0·2	12·5
6·0	1·8	1·5	0·3	16·7
6·4	1·9	1·7	0·2	10·5
6·8	1·9	1·7	0·2	10·5
7·2	2·2	2·0	0·2	9·1
7·5	2·3	2·1	0·2	8·7
7·9	2·4	2·2	0·2	8·3
8·3	2·5	2·3	0·2	8·0
		Uni-electrode (β)		
5·3	2·5	1·4	1·1	44·0
5·6	4·1	2·1	2·0	48·8
6·0	4·9	2·4	2·5	51·0
6·4	5·4	2·7	2·7	50·0
6·8	6·0	3·0	3·0	50·0
7·2	6·9	3·4	3·5	50·0
7·5	7·7	3·8	3·9	50·7
7·9	8·6	4·2	4·4	51·6
8·3	8·9	4·6	4·3	48·8

3. Joshi[2, 3, 4] has shown as a general result that Δi occurs predominantly in the high frequency part of the conductivity produced under the discharge. It is seen from the experimental arrangement that the current picked up by the aerial is chiefly in the H.F. The fundamental significance of the threshold potential V_m (and its dependence on factors such as the structural constants of the tube, the frequency of the A.C. supply) above which only Δi occurs has been established by Joshi.[5, 6] It was interesting to observe that in the present case, V_m was found to be 4·3 kV, in both the *uni-* and the *bi*-electrode excitations, *i.e.*, in (α) and (β) respectively. For the same applied potential V in (α) and (β), i should have been the same, since according to a general result due to Joshi,[7] *ceteris paribus*, i depends on $V\text{-}V_m$. The results in Table I show, however, that i in (α) is far smaller than in (β). Thus *e.g.*, at 6 kV i_d is 4·9 and 1·8 units, corresponding to (β) and (α), respectively. This disparity is explicable on the following considerations:

In (α) the bi-electrode excitation, the two electrodes, are constantly out of phase by π, with possibly a neutral zone in the discharge space corresponding to the earthed centre on the transformer secondary. As a consequence, the earth connected aerial receives two half wave trains mutually out of phase by π which are, therefore, subject to interference. Under ideal conditions the aerial current would be nil; actually, however, the two halves of the circuit are not strictly equivalent in respect of their oscillatory constants; of the position of the neutral zone due to the asymmetry of the excited system, etc. It was also remarkable to find that both the net and the relative *Joshi-effect* Δi and $\% \Delta i$, are far greater in (β) as compared with (α); thus *e.g.*, at 6 kV in (α) Δi and $\% \Delta i$ are 0·3 and 16·7 as against 2·5 and 51 in (β), respectively. The current in *bi*-electrode excitation (α) being much smaller than that in *uni*-electrode excitation (β), it is to be anticipated that the same should hold for the corresponding Δi and $\% \Delta i$ in (α), since according to a general result due to Joshi,[2] both the above quantities increase with i over a certain limited range of applied potentials, and decrease thereafter.

Joshi[8] has suggested recently a following (additional) factor in the production of Δi. It is that irradiation produces a change of capacity and therefore, that of phase between the electrodes. On this view, it is easy to see that under irradiation, in effect, the interelectrode phase in the *uni*-electrode excitation shifts towards that normal in a *bi*-electrode excitation (that is, in dark); as a consequence of this phase-shift, the photo-reduction of conductivity as observed, follows. Also, since in the latter, *i.e.*, *bi*-electrode excitation neither of the electrodes has a constant characteristic

phase, like the earth electrode in the *uni*-electrode excitation, the phase-shift[8] under light at either electrode as contemplated by Joshi is less likely; the corresponding *Joshi-effect* is anticipated, therefore, to be smaller than in *uni*-electrode excitation, as observed.

In conclusion, I express my grateful thanks to Prof. S. S. Joshi, D.Sc. (Lond.), for suggesting the problem and for the keen interest he took during the work.

Summary

Production of *Joshi-effect* Δi, *viz.*, an instantaneous and reversible photo-diminution of current i in excited chlorine has been studied in an *aerial* current under *uni-*, and *bi*-electrode excitation. The current in dark, the net and relative *Joshi-effect* Δi and $\%\ \Delta i$, in the latter, were comparatively low. Based on interference of anti-phase wave trains, together with a recently suggested *phase-shift* due to Prof. Joshi in the production of this effect, an explanation is developed for the reduced i (in dark), Δi and $\%\ \Delta i$ under *bi*-electrode excitation.

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A NEW IDENTICAL EQUATION FOR MULTIPLICATIVE FUNCTIONS OF TWO ARGUMENTS AND ITS APPLICATIONS TO RAMANUJAN'S SUM $C_M(N)$*

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I. Introduction

In his memoir[1] "The Theory of Multiplicative Arithmetic Functions," Dr. Vaidyanathaswamy establishes an identical equation,[2] for any multiplicative function $f(M_1, \ldots, M_r)$ of r arguments which in the case of functions of one argument reduces to

$f(MN) = f(M) f(N) \cdot C(M, N)$, where $C(M, N)$ is a cardinal function defined by $C(M, N) = (-1)^{\gamma} f^{-1}(MN)$ if M, N have the same γ distinct prime factors, and $C(M, N) = 0$, otherwise.

But the above identical equation is not always the most suitable one, for multiplicative functions of two arguments. In this paper, I derive a new identical equation for functions of two arguments. The special interest of this equation lies in its applications to Ramanujan's function $C_M(N)$.[3]

We will require the following definitions and notations.[4]

1.1. An arithmetic function $f(M_1, \ldots, M_r)$ of r arguments is said to be multiplicative, if $f(M_1, \ldots, M_r)\, f(N_1, \ldots, N_r) = f(M_1N_1, \ldots M_rN_r)$ whenever the products $\prod_{i=1}^{r} M_i$ and $\prod_{i=1}^{r} N_i$ are mutually prime. (1.1.1) With the convention that unity is both prime to and a factor of every number, it follows that if $f(M_1, \ldots, M_r)$ is multiplicative in $M_1, \ldots, M_r$, then $f(1, 1, \ldots, 1) = 1$.

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* Some of the results of this paper were given in a thesis, for which the M.Sc. Degree of the University of Madras, was awarded, and I am deeply indebted to Dr. Vaidyanathaswamy for his guidance.

[1] See *Trans. Amer. Math. Soc.*, 33, No. 2, 579–662, 1931. The above memoir, will be hereafter, referred to as *M.F.*

[2] See *M.F.*, p. 645.

[3] *Collected Papers of Srinivasa Ramanujan*, 179–80.

[4] For details ref. *M.F.*

1.2. *The generating series:*—The series,

$$f_p(x_1, \ldots, x_r) = \sum_{\substack{m_i = 0 \\ (i = 1, 2, \ldots r)}}^{\infty} f(p^{m_1}, \ldots, p^{m_r})\, x_1^{m_1} \ldots x_r^{m_r}$$

is called the generating series or briefly *g*-series of the multiplicative function f to the prime base p. Given the *g*-series to all prime bases, it follows that the multiplicative function is completely determined.

1.3. *Convolution:*—Let $f(M_1, \ldots, M_r)$ be a multiplicative function of $r(>1)$ arguments. Then, the process of convolving M_1, M_2 in f consists in forming the function,

$$\phi(M, M_3, \ldots, M_r) = \sum_{M_1 M_2 = M} f(M_1, M_2, \ldots, M_r).$$

ϕ can readily seen to be a multiplicative function of its $(r-1)$ arguments and its *g*-series to a prime base p is given by,

$$\phi_{(p)}(x, x_3, \ldots x_r) = \Sigma \Big(\sum_{m_1 + m_2 = m} a_{m_1, m_2, \ldots m_r} \Big) x^m x_3^{m_3} \ldots x_r^{m_r}$$

$$= f_{(p)}(x, x, x_3, \ldots x_r), \text{ where}$$

$$f_{(p)}(x_1, x_2, \ldots x_r) = \Sigma\, a_{m_1, m_2, \ldots m_r}\, x_1^{m_1} \ldots x_r^{m_r}$$

is the *g*-series of f to the base p. The function ϕ is called *a convolute* of f. In particular, for functions $f(M_1, M_2)$ of two arguments, *the* convolute ϕ is given by $\phi(M) = \sum_{d \mid M} f\left(\frac{M}{d}, d\right)$. We will denote $\phi(M)$ by $\Omega f(M_1, M_2)$.

(1.3.1) The composite of two multiplicative functions $f_1(M_1, \ldots, M_r)$, $f_2(M_1, \ldots, M_r)$ is the function $f(M_1, \ldots, M_r)$, obtained by convolving the pairs M_i, N_i in the product, $f_1(M_1, \ldots M_r) \times f_2(N_1, \ldots N_r)$. Thus $f(M_1, \ldots M_r) = \Sigma f_1\left(\frac{M_1}{d_1}, \ldots, \frac{M_r}{d_r}\right) f_2(d_1, \ldots, d_r)$ summed for all divisors d_i of M_i, $(i = 1, 2, \ldots r)$. f is denoted by $(f_1 \cdot f_2)$ and its *g*-series to any base p is given by, $f_{(p)}(x_1, \ldots, x_r) = f_{1(p)}(x_1, \ldots x_r) \times f_{2(p)}(x_1, \ldots, x_r)$. (1.3.2) The composite of $f(M_1, \ldots, M_i, M_{i+1}, \ldots M_r)$ and $E_0(M_1, \ldots, M_i)\, E(M_{(i+1)}, \ldots M_r)$ is called the *integral* of f with respect to $M_{i+1}, \ldots, M_r$, where $E_0(M_1, \ldots M_r)$ and $E(M_1, \ldots M_r)$ are functions defined by,

$$E_0(M_1, \ldots, M_r) = 1, \text{ when } M_1 = M_2 = \ldots = M_r = 1 \text{ and}$$

$$= 0, \text{ otherwise}$$

and $$E(M_1, \ldots, M_r) = 1, \text{ for all values of } M_1, \ldots M_r.$$

The composite of $f(M, N)$ with $\psi(M)$ is the same as $f(M, N)$. $\psi(M)\, E_0(N)$.

(1.3.3) If $f_1(M_1, M_2)$ and $f_2(M_1, M_2)$ are multiplicative in M_1, M_2, then it can be easily shown that $(\Omega f_1).(\Omega f_2) = \Omega(f_1 . f_2)$.

(1.3.4) The inverse of f denoted by f^{-1} is the unique function, determined from $f(M_1, \ldots M_r) \cdot f^{-1}(M_1, \ldots M_r) = E_0(M_1, \ldots, M_r)$. It follows readily that $f_{(p)}(x_1, \ldots x_r) \times f_{(p)}^{-1}(x_1, \ldots, x_r) = E_{0(p)}(x_1, \ldots, x_r) = I$.

(1.3.5) The inverses of $E_0(M)$, $E(M)$ and $I(M)$ [the function defined by $I(M) = M$], can be easily seen to be $E_0(M)$, $\mu(M)$ and $M\mu(M)$ respectively, $\mu(M)$ being the well-known Möbius function, defined thus:—

$\mu(1) = 1$, $\mu(M) = 0$ if M has a squared factor and

$\mu(p_1 p_2 \ldots p_r) = (-1)^r$ if $p_1, p_2, \ldots, p_r$ are different primes.

(1.3.6) The following properties of the processes of composition and inversion will be often used in the sequel:—

(*a*) Composition is associative and commutative.

(*b*) The compositional operation distributes multiplication, whenever the multiplier is a linear function.

(*c*) The inverse of the composite of any number of functions is the composite of their inverses.

(*d*) The inverse of the product of functions without common argument is the product of the inverses. For *e.g.*, $[\phi(M)\psi(N)]^{-1}$ is $\phi^{-1}(M)\psi^{-1}(N)$.

(*e*) In a compositional equation, any term can be transposed from one side to the other, by replacing it by its inverse. Thus if $f_1 \cdot f_2 = \phi_1 \cdot \phi_2$, then $f_1 = \phi_1 \cdot \phi_2 \cdot f_2^{-1}$.

(1.3.7). The *derivate* of a function $f(M, N)$ with respect to M is defined as $f(1, N)$ and is denoted by $D_M(f)$; $D_M(f)$ is clearly multiplicative in N. Also, it can be easily seen that for two functions $f(M, N)$, $\phi(M, N)$,

(*a*) $D_M(f) \cdot D_M(\phi) = D_M(f \cdot \phi)$ and (*b*) $D_M(f^{-1}) = \{D_M(f)\}^{-1}$

1.4. A *cardinal* function $C(M, N)$ is one for which $D_M(C) = E_0(N)$ and $D_N(C) = E_0(M)$. It is easy to show that (*a*) the composite of two cardinal functions is a cardinal function and (*b*) the inverse of a cardinal function is a cardinal function.

1.5. A *principal* function $P(M, N)$ is one which vanishes whenever M is not equal to N. The function $\psi(M) = P(M, N)$ is called the function of one argument equivalent to the principal function $P(M, N)$.

(1.5.1) If $\psi_p(x)$ be the *g*-series of ψ to a base *p*, then $P_p(x, y) = \psi_p(xy)$. Thus ψ determines $P(M, N)$ completely and we will write $P = \text{princ } \psi$.

(1.5.2) It can be easily seen that, (*a*) ϕ (M, N) $\times$ princ ψ = princ [ϕ (M, M) $\times$ ψ (M)], ϕ (M, N), being any multiplicative function of M, N. and (*b*) (princ ψ)$^{-1}$ = princ ψ^{-1}.

2. Next, before proceeding to the main results of the paper, we will establish three lemmas which will be required later.

2.1. *Lemma.*—Every multiplicative function F (M, N) of two arguments, possesses, with respect to each of its arguments, the following property, which may be referred to as 'quasi-multiplicative' property:—

Wherever M is prime to M', F (M, N) F (M', N) = F (MM', N) F (1, N).

Similarly, F (M, N) F (M, N') = F (M, NN') F (M, 1) if N and N' are mutually prime.

We will prove the first part.

Proof.—Let $N = N_1N_2T$, where N_1 contains only all those prime factors of N, which divide M and further these prime factors occur in N_1, to the same powers, to which they occur in N; N_2 is composed of only those prime factors of N, which divide M[1] and these occur in N_2, to the same powers to which they occur in N; and, T is composed of the remaining prime factors of N (to the same powers to which they occur in N).

Such a resolution is clearly possible.

Now[5] $(N_1, N_2) = (N_2, T) = (N_1, T) = 1$ $\because$ $(M, M') = 1$

Also $(N_1, N_2T) = (MN_1, N_2T) = (MN_1, M'N_2T) = 1$

Therefore $F(M, N) = F(M, N_1N_2T) = F(M, N_1)\, F(1, N_2T)$

and $F(M', N) = F(M', N_1N_2T) = F(M', N_2T)\ F(1, N_1)$.

Hence $F(M, N)\, F(M', N) = F(M, N_1)\, F(1, N_2T)\, F(M', N_2T)\, F(1, N_1)$

$= F(M, N_1)\, F(M', N_2T)\, F(1, N_2T)\, F(1, N_1)$

$= F(MM', N_1N_2T)\, F(1, N_1N_2T)$

$= F(MM', N)\, F(1, N)$.

The second part can be proved similarly.

2.2. *Lemma.*—The necessary and sufficient condition that a multiplicative function F (M, N) of the two arguments M, N should be multiplicative in one of the arguments (say) M is $D_M(F) = E(N)$.

Proof.—The condition is necessary, for if F (M, N) is to be multiplicative in M, then F (1, N) F (M, N) = F (M, N) by (1.1.1)

---

[5] (*a*, *b*) denotes the greatest common divisor of *a* and *b*.

or $F(1, N) = 1 = E(N)$

(*i.e.*) $D_M(F) = E(N)$.

The sufficiency of the condition follows from lemma 2.1 since if $D_M(F) = E(N)$, then $F(M, N) F(M', N) = F(MM', N)$ whenever $(M, M') = 1$.

2.3. *Lemma.*—If a multiplicative function $F(M_1, M_2)$ is of the form $f(M_1) f^{-1}(M_2)$ then $\Omega F(M_1, M_2) = E_0(M)$.

For, $\Omega F(M_1, M_2) = \sum_{d/M} f\left(\frac{M}{d}\right) f^{-1}(d) = f \cdot f^{-1} = E_0(M)$.

We will now derive,

3. *The new identical equation for multiplicative functions of two arguments.*

Let $F(M, N)$ be multiplicative in M and N. Then $F(M, 1) F(1, N)$ is also multiplicative in both the arguments. We know by (1.3.4) that every multiplicative function $F(M, N)$ has an inverse $F^{-1}(M, N)$ such that $F(M, N) \cdot F^{-1}(M, N) = E_0(M, N)$.

The inverse of $F(M, 1) F(1, N)$, by (1.3.6) (*d*) and (1.3.7) (*b*) is $F^{-1}(M, 1) F^{-1}(1, N)$ and we have

$$F(M, N) . F^{-1}(M, N) = E_0(M, N) = F(M, 1) F(1, N) \cdot F^{-1}(M, 1) F^{-1}(1, N).$$

Therefore by (1.3.6) (*e*)

$$F(M, N) = F(M, 1) F(1, N) \cdot \{F^{-1}(M. 1) F^{-1}(1, N) . F(M, N)\}$$

or 3.1 $$F(M, N) = F(M, 1) F(1, N) \cdot C(M, N),$$

where $$C(M, N) = F(M, N) \cdot F^{-1}(M, 1) F^{-1}(1, N).$$

Now $$D_M(C) = F(1, N) \cdot F^{-1}(1, N) = E_0(N)$$ by (1.3.7) (*a*)

Similarly $$D_N(C) = E_0(M).$$

Hence $C(M, N)$ is a cardinal function. We shall refer to $C(M, N)$ as the *cardinal component* of $F(M, N)$ and the relation 3.1, as the *identical equation* of $F(M, N)$.

It easily follows from 1·4 (*a*) and (*b*) that (a) *the cardinal component of the composite of two functions is the composite of their cardinal components and* (b) *the cardinal component of the inverse of a function is the inverse of its cardinal component.*

(3.1.1) THEOREM.—*The cardinal components of a cardinal function and a principal function are identical with the functions themselves.*

For, if $F(M, N)$ is cardinal or principal, then $F(M, 1) = E_0(M)$; $F(1, N) = E_0(N)$ and therefore

$$F(M, N) = E_0(M) E_0(N) \cdot C(M, N) = E_0(M, N) \cdot C(M, N) = C(M, N).$$

When the cardinal component $C(M, N) = E_0(M, N)$, we deduce the following important result:—

(3.1.2) THEOREM.—*The necessary and sufficient condition that a multiplicative function $F(M, N)$ be a product of two functions of M, N respectively is that its cardinal component $C(M, N) = E_0(M, N)$.*

Proof.—Suppose $F(M, N) = F_1(M) F_2(N)$. Then clearly $F_1(M) = F(M, 1)$ and $F_2(N) = F(1, N)$, so that

$$F(M, N) = F(M, 1) F(1, N).$$

Therefore $C(M, N) = F(M, N) \cdot F^{-1}(M, 1) F^{-1}(1, N)$

$$= F(M, 1) F(1, N) . F^{-1}(M, 1) F^{-1}(1, N) = E_0(M, N).$$

The sufficiency of the condition is obvious, from 3.1.

Note.—It follows from the above that the *cardinal component* represents in the general case, the *deviation* of $F(M, N)$ from the product-form.

(3.1.3). *The identical equation for functions of a single-argument.*—If $F(M, N)$ is a function of the product of the arguments and is equal to $f(MN)$, then the new identical equation reduces to Dr. Vaidyanathaswamy's identical equation for functions of a single argument.

(3.1.4) *The Busche-Ramanujan identity for functions of a single argument.*[6]—If $F(M, N) = f(MN)$ and the cardinal component is a principal function, then the new identical equation assumes the form of a Busche-Ramanujan identity for functions of a single argument.

For, if $C(M, N) = \text{princ } \psi$, then $F(M; N) = f(MN)$

$$= f(M) f(N) . C(M, N)$$

$$= \sum_{d/M} \sum_{\delta/N} f\left(\frac{M}{d}\right) f\left(\frac{N}{\delta}\right) C(d, \delta)$$

$$= \sum_{d/M, N} f\left(\frac{M}{d}\right) f\left(\frac{N}{d}\right) \psi(d)$$

(summed for common-divisors d, of M, N), which is the form of the abovementioned identity.

3.2. *The cardinal components of the Ordinal and the Modular functions.*—We will next examine the nature of the cardinal components of two important types of multiplicative functions of two arguments, *viz.*, (1) the Ordinal and (2) the Modular functions.

---

[6] See *M.F.*, p. 646.

Definitions.—A multiplicative function $f(M, N)$ is called an *ordinal* function, if it vanishes whenever $N > M$. M, N are called the *major* and the *minor* arguments respectively, of the ordinal function.

If a multiplicative function $f(M, N)$ has its value unaltered whenever N is increased by any multiple of M, it is said to be a *modular* function. M is called the *modulus*.

I have shown elsewhere[7] that (a) *the composite of two Ordinal functions is an Ordinal function*, and (b) *corresponding to any Modular function* f (M, N), *there exists a unique Ordinal function* $\psi(M, N)$, (*called the* primitive *of* f) *such that* f *is the integral of* ψ *with respect to its minor argument N.*

We will assume the above results in what follows:—

(3.2.1) THEOREM. *The cardinal component of an Ordinal function is itself an Ordinal function.*

Proof.—For, let $f(M, N)$ be an Ordinal function. Then $f(1, N) = E_0(N)$ since $f(1, N) = 0$ whenever $N > 1$. The identical equation of $f(M, N)$ is, by (3·1)

$$f(M, N) = f(M, 1)\, E_0(N).C(M, N), \text{ where}$$

$$C(M, N) = f(M, N).f^{-1}(M, 1)\, E_0(N).$$

But $f^{-1}(M, 1)\, E_0(N)$ is an Ordinal function since if $N > M$, it implies that $N > 1$ and so the function vanishes. Hence $C(M, N)$ being the composite of two Ordinal functions is Ordinal by 3.2 (*a*).

(3.2.2) THEOREM.—*The cardinal component of a Modular function is Ordinal and identical with that of its primitive.*

Proof.—Let $f(M, N)$ be a modular function and $\psi(M, N)$ be its primitive so that $f(M, N) = \psi(M, N).E_0(M)\, E(N)$ by 3.2 (*b*).

Now $f(1, N) = f(1, 1)$, on account of the modular character of $f(M, N)$

$$= E(N)$$

and $D_N(f) = D_N(\psi) \cdot D_N\{E_0(M)\, E(N)\}$ by (1.3.7) (*a*)

(*i.e.*), $f(M, 1) = \psi(M, 1) \cdot E_0(M) = \psi(M, 1)$.

The identical equation of $\psi(M, N)$ is given by

$$\psi(M, N) = \psi(M, 1)\, E_0(N) \cdot C(M, N), \text{ where } C(M, N) \text{ is Ordinal by (3.2.1).}$$

---

[7] Under publication in *J.I.M.S.*

Therefore $f(M, N) = \psi(M, N).E_0(M)\ E(N)$

$= \psi(M, 1)\ E_0(N).C(M, N).E_0(M)\ E(N)$

$= \psi(M, 1)\ E_0(N).E_0(M)\ E(N).C(M, N)$

$= \psi(M, 1)\ E(N).C(M, N)$

$= f(M, 1)\ E(N).C(M, N)$

Hence by (3.1) it follows that the cardinal component of f is Ordinal and identical with that of its primitive.

(3.2.3). We will now give some illustrations of the identical equation: *The identical equation of the elementary function* $\delta(M, N)$. This is defined by,

$$\delta(M, N) = 1 \text{ if } N/M$$
$$= 0, \text{ otherwise.}$$

It is clear that $\delta(M, N) = 0$ if $N > M$ and can be easily shown to be multiplicative in M, N. Thus it is an Ordinal function. Now, the identical equation of $\delta(M, N)$ is given by,

$$\delta(M, N) = \delta(M, 1)\ E_0(N).C(M, N)$$
$$= E(M)\ E_0(N).C(M, N).$$

Therefore $C(M, N) = \delta(M, N).\mu(M)\ E_0(N).$

Let $\delta_{(p)}(x, y)$ be the g-series of $\delta(M, N)$ to any base p so that

$$\delta_{(p)}(x, y) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \delta(p^m, p^n)\, x^m\, y^n$$

$$= \sum_{m=0}^{\infty} x^m\, [1 + y + \ldots + y^m]$$

Now $\mu_{(p)}(x)\ E_0(y) = 1 - x.$

Hence $C_p(x, y) = (1 - x)\left[\sum_{m=0}^{\infty} x^m (1 + y \ldots + y^m)\right]$ See (1.3.1)

$= 1 + xy + x^2y^2 + \ldots + x^m y^m + \ldots$; on reduction

$= P_p(x, y)$ where $P(M, N) = \text{princ } E$ [ref. (1.5.1)].

Therefore $C(M, N) = \text{princ } E$ and the identical equation of $\delta(M, N)$ becomes, $\delta(M, N) = E(M)\ E_0(N), \cdot \text{princ } E.$

NOTE.—*If* $\psi(M)$ *is the convolute of* $\delta(M_1, M_2)$, *then* ψ *represents the number of square divisors of* M.

For, $\psi(M) = \Omega\,\delta(M_1, M_2) = \Omega\,[E(M_1)\,E_0(M_2).\text{princ E}]$

$= \Omega\,E(M_1)\,E_0(M_2).\Omega\,\text{princ E}$, by (1.3.3)

$= E(M).\lambda(M)$, where $\lambda(M) = \Omega\,\text{princ E}$

$= 1$ if M is a perfect square and

$= 0$, otherwise.

$= \Sigma\lambda(d^2)$, summed for the square divisors of M

= the number of square divisors of M, since $\lambda(d^2) = 1$.

(3·2·4) *The trigonometric function* $T(M, N)$

$T(M, N)$ is defined as $\sum_{h=1}^{N} e^{\frac{2\pi i h M}{N}}$ and it is well known from Trigonometry that $T(M, N) = N$ if N/M,

$= 0$, otherwise.

Hence $T(M, N) = N\delta(M, N)$ and is therefore multiplicative in M, N. The identical equation of $T(M, N)$ is thus given by

$$T(M, N) = N\delta(M, N) = N\,[E(M)\,E_0(N)\cdot\text{princ E}]$$

$$= E(M)\,N\,E_0(N).N\,\text{princ E by (1.3.6) } (b)$$

$$= E(M)\,E_0(N).\text{princ I by (1.5.2). } (a)$$

It can also be easily shown that $\Omega T(M_1, M_2)$ represents the sum of the square divisors of M.

4. We will next proceed to *the applications of the identical equation to Ramanujan's trigonometric sum* $C_M(N)$.

This sum is defined as $C_M(N) = \sum_h e^{\frac{2\pi i h N}{M}}$, where h runs through a complete set of residues prime to M. Ramanujan expressed $C_M(N)$ in the form

$$C_M(N) = \sum_{d/M,\,N} \mu\left(\frac{M}{d}\right) d = \sum_{d/g\,=\,(M,\,N)} \mu\left(\frac{M}{d}\right) d \qquad (A)$$

and Hardy[8] has shown that

$$C_M(N)\,C_{M'}(N) = C_{MM'}(N) \text{ whenever } (M, M') = 1$$

(*i.e.*) $C_M(N)$ is multiplicative in M.

---

[8] *An Introduction to the Theory of Numbers*, Hardy and Wright, p. 56, Theorem 67

But from (A) it can be easily seen that $C_M(N)\,C_{M'}(N') = C_{MM'}(NN')$ whenever $(MN, M^1N^1) = 1$.

Hence $C_M(N)$ is multiplicative in both the arguments. Also it is clear that $C_M(N) = C_M(N + \lambda M)$.

Therefore $C_M(N)$ is a modular function.

Now $C_1(N) = 1 = E(N)$. Hence from Lemma (2.2) we have $C_M(N)\,C_{M'}(N) = C_{MM'}(N)$ if $(M, M') = 1$. Thus the multiplicative property of $C_M(N)$ in M, follows as a consequence of it being a modular function.

Again, $C_M(1) = \mu(M)$ from (A) and therefore by the second part of lemma (2.1),

$$C_M(N)\,C_M(N') = \mu(M)\,C_M(NN') \text{ whenever } (N, N') = 1.$$

It is also readily seen from (A) that $C_M(N) = C_M(g)$ (B)

4.1. *The identical equation of $C_M(N)$.*—Because $C_M(N)$ is a multiplicative function of two arguments, by 3·1, it satisfies an identical equation given by, $C_M(N) = C_M(1)\,C_1(N).C(M, N)$

$$= \mu(M)\,E(N).C(M, N)$$

$$= E^{-1}(M)\,E(N).C(M, N).$$

But the right side of relation 4. (A) is the same as $E^{-1}(M)E(N)$.princ I. Hence $C(M, N) =$ princ I so that the identical equation becomes,

$$C_M(N) = E^{-1}(M)\,E(N)\cdot \text{princ I}.$$

We will now derive some important properties of Ramanujan's function using its identical equation.

(4.1.1) THEOREM.—*$\Sigma\, C_d(N) = M$ if M/N.*

$= 0$, otherwise,

the summation on the left being for all the divisors of M.

Proof.—For $\sum_{d/M} C_d(N) = C_M(N).E(M)\,E_0(N)$, ref. (1.3.2)

$$= E^{-1}(M)\,E(N).\text{princ I}\cdot E(M)\,E_0(N)$$

$$= E^{-1}(M)\,E(N).E(M)\,E_0(N)\cdot \text{princ I using (1.3.6)}\,(a)$$

$$= E_0(M)\,E(N).\text{princ I}$$

$$= \sum_{d/M,\,N} E_0\left(\frac{M}{d}\right) E\left(\frac{N}{d}\right) a$$

$$= M \text{ if } M/N \text{ and } 0, \text{ otherwise,}$$

(4.1.2). THEOREM.—*$\Sigma C_M(r) = E_0(M)$, where r runs through a complete set of residues mod. M.*

Proof.—We have seer, 4 (B) that $C_M(N) = C_M(g)$. Now, let $t_1 = 1$. t_2, $t_3 \ldots, t_k = M$ be the distinct divisors of M. Then Dr. Vaidyanathaswamy[9] has shown that the integers 1, 2, ... M can be divided into classes $C_1, \ldots, C_k$ such that C_i contains those numbers whose g.c.d. with M is t_i. The class C_i will contain $\phi\left(\frac{M}{t_i}\right)$ numbers, (ϕ being Euler's function).

Now $\sum_r C_M(r) = \sum_{s=1}^{M} C_M(r)$

Hence $\sum_r C_M(r) = \sum_{d|M} C_M(d)\,\phi\left(\frac{M}{d}\right) = \psi(M, M)$, where

$$\psi(M, N) = C_M(N).E_0(M)\,\phi(N) = E^{-1}(M)\,E(N)\cdot \text{princ I}.E(M)\,\phi(N)$$

or $$\psi(M, N) = E^{-1}(M)\,[(\phi.E)(N)].\text{princ I}$$

$$= \mu(M)\,I(N)\cdot \text{princ I} = \sum_{d|M,\,N} \mu\left(\frac{M}{d}\right)\frac{N}{d}\,d$$

$$= N \sum_{d|M,\,N} \mu\left(\frac{M}{d}\right)$$

Hence $\psi(M, M) = M \sum_{d|M} \mu\left(\frac{M}{d}\right) = M\,[E^{-1}\cdot E] = M\,[E_0(M)] = E_0(M)$

Thus $\sum_r C_M(r) = E_0(M)$.

(4.1.3) THEOREM. *The inverse of $C_M(N)$ is a modular function with N as the modulus and satisfies the relation $C_M^{-1}(N) = \sum_{d|M,\,N} \mu\left(\frac{N}{d}\right)\mu(d)\,d$*

Proof.—For, $C_M^{-1}(N) = [E^{-1}(M)\,E(N)\cdot \text{princ I}]^{-1}$

$= [E^{-1}(M)\,E(N)]^{-1}\cdot(\text{princ I})^{-1}$ by (1.3.6) (*c*)

$= E(M)\,\mu(N)\cdot \text{princ I}^{-1}$ by (1.5.2) (*b*)

or $$C_M^{-1}(N) = \sum_{d|M,\,N} \mu\left(\frac{N}{d}\right)\mu(d)\,d, \qquad \text{See (1.3.5)}$$

$$= \sum_{d|g=(M,\,N)} \mu\left(\frac{N}{d}\right)\mu(d)\,d$$

It follows that

$$C_M^{-1}(N) = C_{M+\lambda N}^{-1}(N) \text{ since } (M, N) = g = (M + \lambda N, N)$$

Thus $C_M^{-1}(N)$ has the modulus N.

---

[9] "A Remarkable property of the integers Mod. N and its bearing on Group-Theory," *Proc. Ind. Acad. Sci.*, 1937, 5, 63–75.

(4.1.4) THEOREM.

$$\sum_{d/M} C_{\frac{M}{d}}(d) = +\sqrt{M} \text{ if } M \text{ is a perfect square,}$$
$$= 0, \text{ otherwise.}$$

Proof.—For, $\sum_{d/M} C_{\frac{M}{d}}(d) = \Omega\, C_{M_1}(M_2) = \Omega\,[E^{-1}(M_1)\, E(M_2).\text{princ } 1]$

$= \Omega\, E^{-1}(M_1)\, E(M_2) \cdot \Omega$ princ I by (1.3.3)

$= E_0(M).\Omega$ princ I using lemma 2.3

$= \Omega$ princ I

$= d$ if $\frac{M}{d} = d$, and 0, otherwise.

Hence the result.

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